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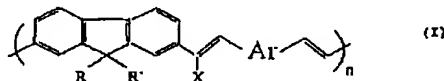
(54) 【発明の名称】 E L素子用フルオレン系重合体及びそれを用いたE L素子

(57) 【要約】

【課題】 製造方法が簡単で、最終物質の構造が明確であり、有機溶媒によく溶解され得る多種の高分子E L材料を提供する。

【解決手段】 一般式 (I)

【化8】



(式中、R、R' は、水素又は炭素数が22までのアルキル基等、Xは水素等、Arは、フェニレン基等、nは1~2, 000の整数を表す) で示されるフルオレン系交互共重合体。

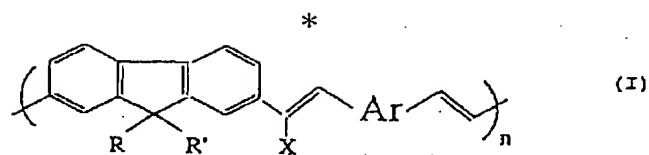
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【特許請求の範囲】

【請求項1】 一般式 (I)

* 【化1】



(式中、R及びR' は、それぞれ水素、炭素数が22個までのアルキル基、シクロアルキル基、アルコキシ基、アルコキシアルキル基、アルコキシアルコキシアルキル基、アルコキシアルコキシアルコキシアルキル基、炭素数が6～18個のアリール基、アリールオキシ基又はア

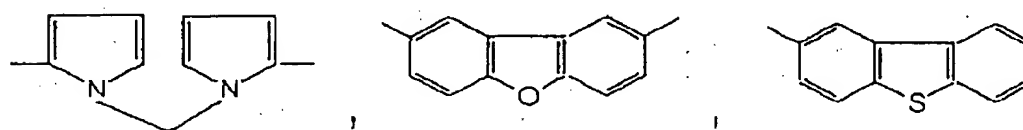
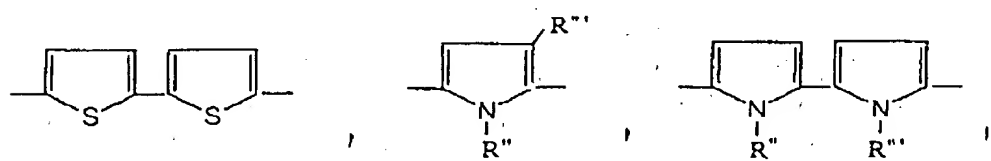
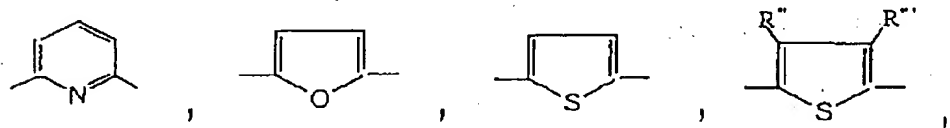
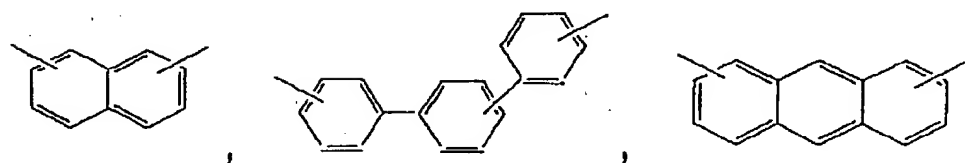
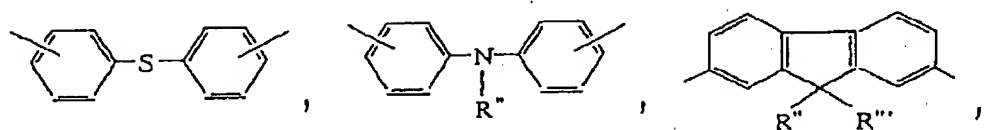
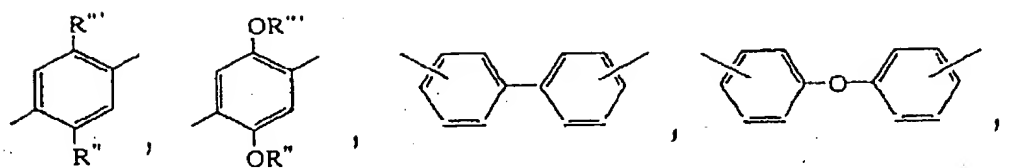
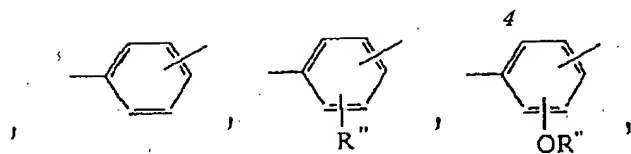
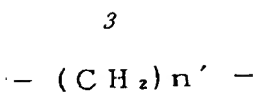
ラルキル基を表し、

Xは、水素又はシアノ基を表し、

Arは、式 (II)

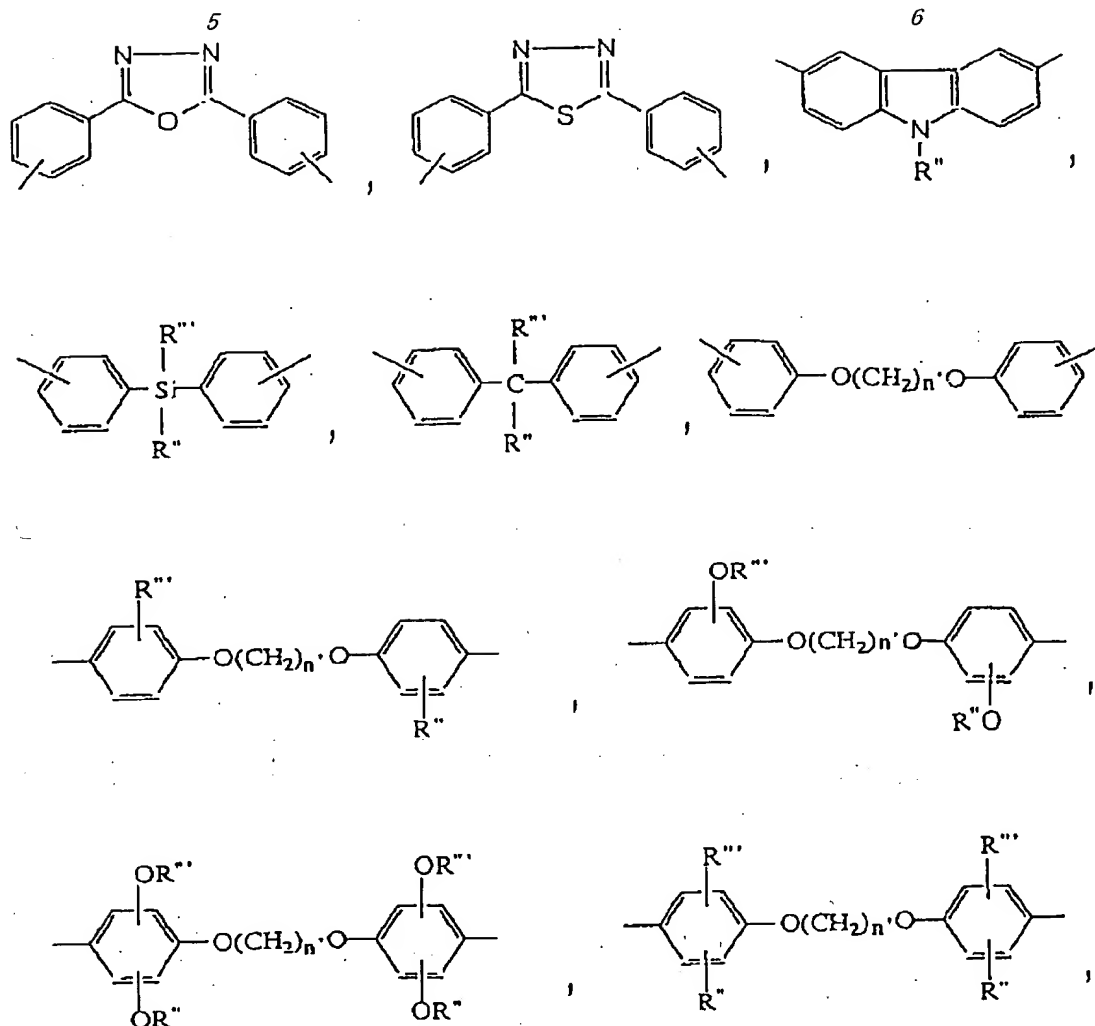
【化2】

(3)



【化3】

(4)



(式中、 R'' 及び R''' は、それぞれ炭素数が22個までのアルキル基、シクロアルキル基、アルコキシ基、アルコキシアルキル基、アルコキシアルコキシアルキル基、炭素数が6～18個のアリール基、アリールオキシ基又はアリール基を表し、 n' は、1～22までの整数を表す)で示される基を表し、 n は、1～2,000の整数を表す)で示されるフルオレン系交互共重合体。

【請求項2】 請求項1記載のフルオレン系交互共重合体を発光層の発光材料として含むEL素子。

【請求項3】 前記の発光材料が、前記のフルオレン系交互共重合体と汎用高分子材料との混合物である請求項2に記載のEL素子。

【請求項4】 前記の汎用高分子材料が、ポリビニルカルバゾール、ポリメチルメタアクリレート、ポリスチレン又はエポキシ樹脂の中から選択される請求項3に記載のEL素子。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、高分子系の電界発光 (Electroluminescence、以下、ELと称する) 素子

の発光材料として用いられるフルオレン系交互共重合体 (Fluorenebased Alternating Copolymers) 及びそれを用いたEL素子に関するものである。

【0002】

【従来の技術】近來、研究されているEL素子は、GaAsのような無機系の半導体であり、該半導体は大きさが小さく、低消費電力のため、現在、小面積のディスプレイ、発光ダイオード (Light Emitting Diode、以下、LEDと称する) ランプ、及び半導体レーザとして用いられている。しかし、このような素子の製造には、高洗浄の工程が必要で、広い面積のLEDを製造することが難しく、効率のよい青色光を得ることも難しいという短所がある。その他、金属化合物の蛍光体イオンが添加された無機半導体及びこれを高分子に分散させた無機系EL素子等もあるが、それらは駆動電圧が高く、高電界で作動するため、半導体の安定性に問題点がある。

【0003】そこで、最近、このような問題点を解決した有機系 (Appl. Phys. Lett., 51, p. 913 (1987)) 及び高分子系 (Nature, 347, p. 539 (1990)) EL材料が開発され、この分野に対する研究が盛んに行われている。即ち、有機染料を蒸着するか (特開平6-13360号及び特開平7-26254号)、又は、共役二重結合を有

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する高分子（国際特許WO92/03491号、WO93/14177号及びWO94/15368号）を陽極と陰極間に置いたEL素子に電圧を掛けると、一般に、陽極側からは正孔が、陰極側からは電子がそれぞれ注入され、それらが発光層に移動して再結合するときに発光する。そして、これらを現在の陰極線チューブ（CRT）、プラズマディスプレイ（PDP）、及び液晶ディスプレイ（LCD）を代替する次世代平板カラーディスプレイ又は電気化学的セル、イメージセンサ、及び光カップラに応用しようとする研究が行われている。

【0004】

【発明が解決しようとする課題】しかし、前記の有機染料を蒸着して製造した素子は、再現性及び均一な薄膜を製造することにおいて問題があり、高分子系素子ではこのような問題がある程度は解決されているが、商業化するには未だ安定性、効率、寿命の点において解決すべき課題が多い。一方、前記の高分子系発光材料としては、ポリフェニレンビニレン（以下、PPVと称する）、ポリチオフェン（以下、PThと称する）、及びポリフェニレン系高分子（Synth. Met., 50 (1-3), p. 491 (1992)、及びAdv. Mater., 4, p. 36 (1992)）等があり、現在このような高分子材料に対する研究が行われているが、有 *

8

* 機溶媒に溶解され得ないという問題がある。更に、適切な置換基を導入して、加工性を向上させ、青色、緑色、及び赤色の多様な色の発光をするPPV及びPTh誘導体（Synth. Met., 62, p. 35 (1994)、Adv. Mater., 4, p. 36 (1994)、及びMacromolecules, 28, p. 7525 (1995)）も提案されているが、その製造工程が複雑で、安定性に問題がある。

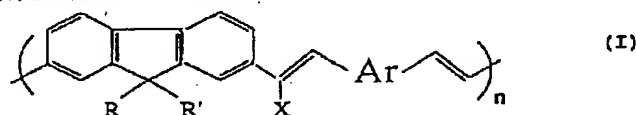
【0005】また、青色の発光をするフルオレン系高分子も提案されている（Jpn. I. Appl. Phys., 30, p. 1941 (1991)）が、これも多様な共役二重結合を有する高分子を製造し得ない物質及びその製造方法を使用していた。そこで、本発明者らは、製造方法が簡単で、最終物質の構造が明確であり、有機溶媒によく溶解され得る多種類の高分子EL材料を製造するため研究を重ねた結果、本発明を完成するに至った。

【0006】

【課題を解決するための手段】本発明に係る高分子系EL素子の発光材料として用いられるフルオレン系交互共重合体は次の一般式（I）により表示される。

【0007】

【化4】



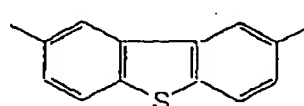
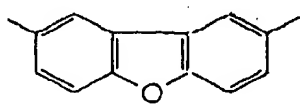
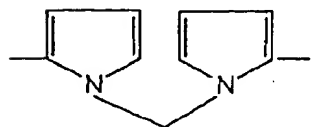
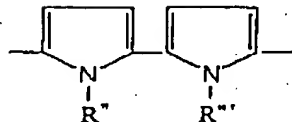
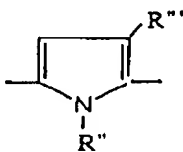
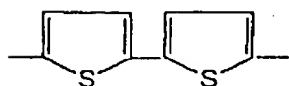
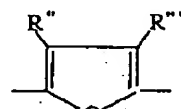
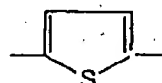
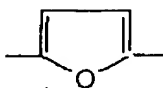
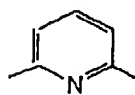
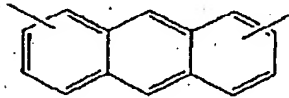
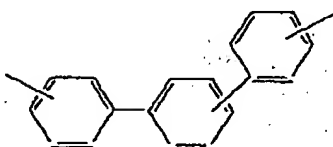
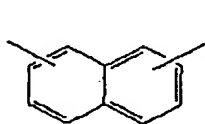
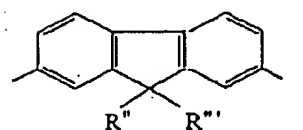
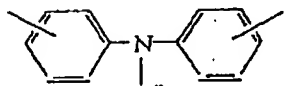
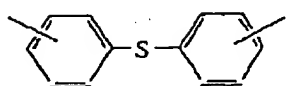
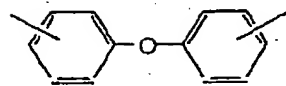
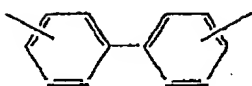
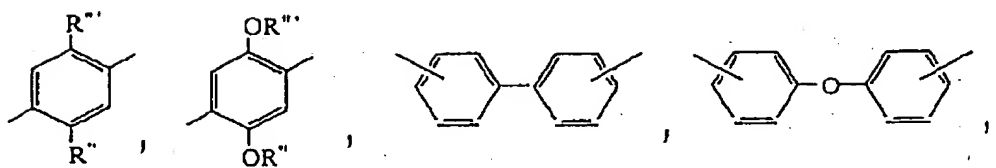
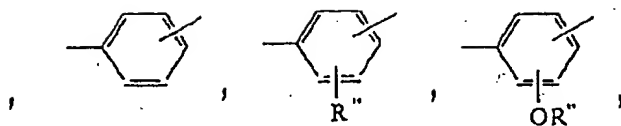
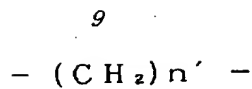
【0008】（式中、R及びR' はそれぞれ水素、炭素数が22個までのアルキル基、シクロアルキル基、アルコキシ基、アルコキシアルキル基、アルコキシアルコキシアルキル基、アルコキシアルコキシアルコキシアルキル基、炭素数が6～18個のアリール基、アリールオキシ基、又はアラルキル基を表し、例えば、メチル、エチル、プロピル、イソプロピル、ブチル、イソブチル、ペンチル、ヘキシル、エチルヘキシル、ヘプチル、オクチル、イソオクチル、ノニル、デシル、ドデシル、ヘキサ

デシル、オクタデシル、ドコデシル、シクロプロピル、シクロペンチル、シクロヘキシル、メトキシ、エトキシ、ブトキシ、ヘキシルオキシ、メトキシエトキシエチル、メトキシエトキシエトキシエチル、フェニル、フェノキシ、トリル、ベンジル、ナフチル、アントリル等を表し、Xは、水素又はシアノ基を表し、Arは下記式

【0009】

【化5】

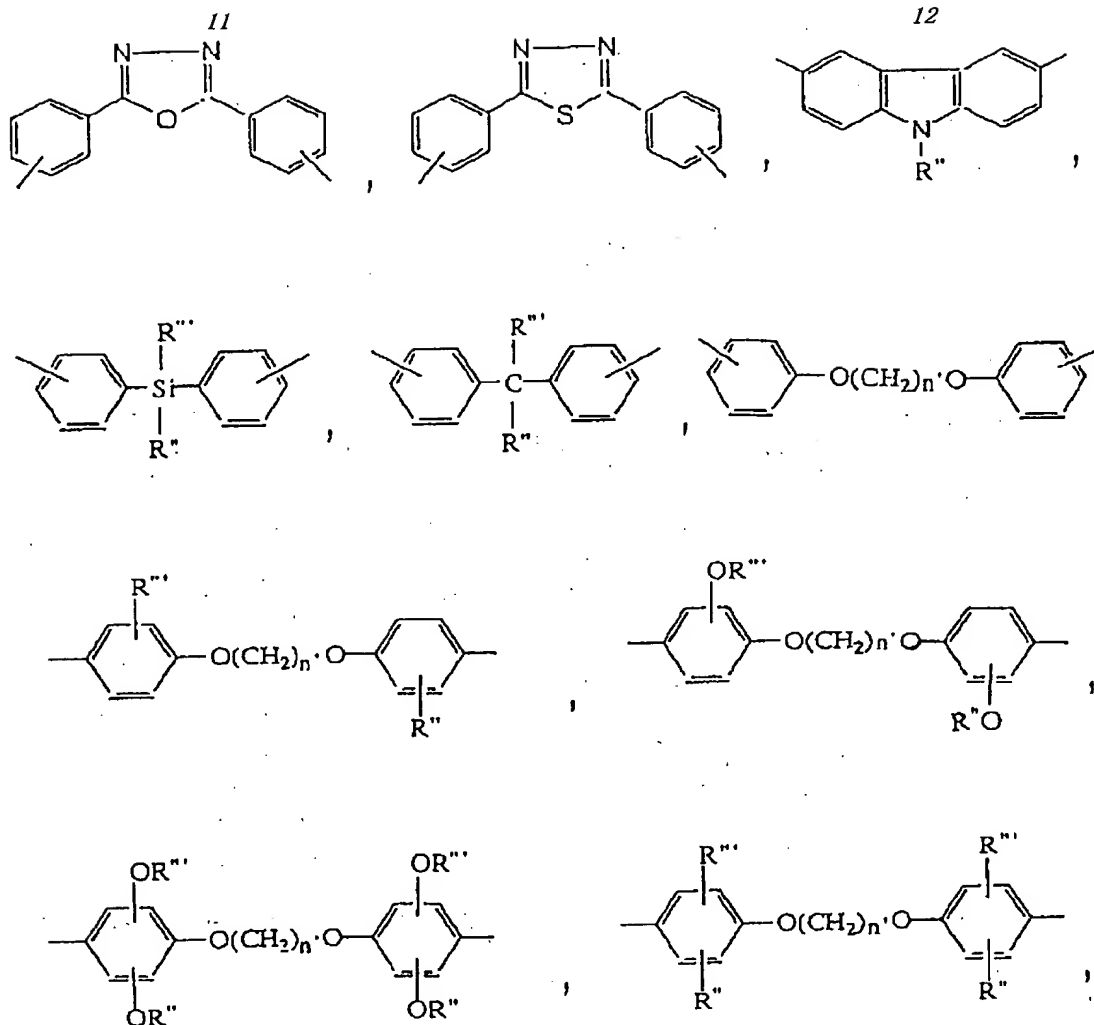
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【0010】

【化6】

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【0011】(式中、 R'' 及び R''' は、それぞれ炭素数が2個までのアルキル基、シクロアルキル基、アルコキシ基、アルコキシアルキル基、アルコキシアルコキシアルキル基、アルコキシアルコキシアルコキシアルキル基、炭素数が6～18個のアリール基、アリールオキシ基又はアラルキル基を表し、 n' は1～22の整数を表す)で示される基を表し、 n は1～2, 000の整数を表す)

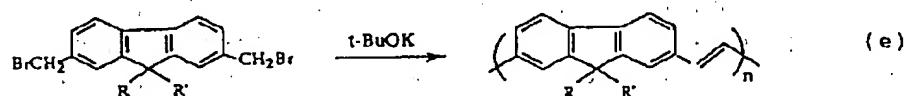
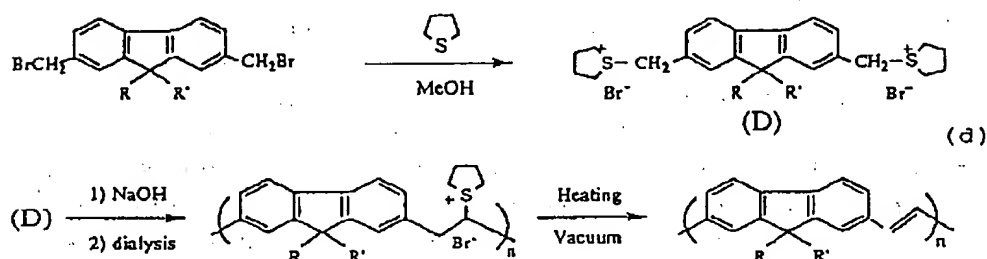
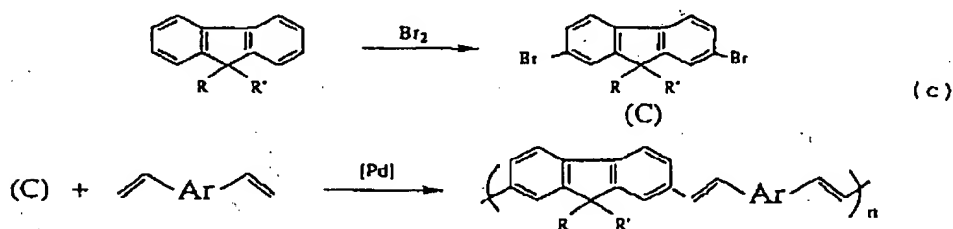
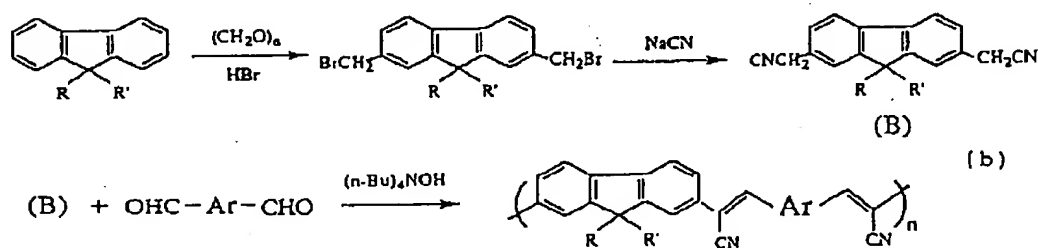
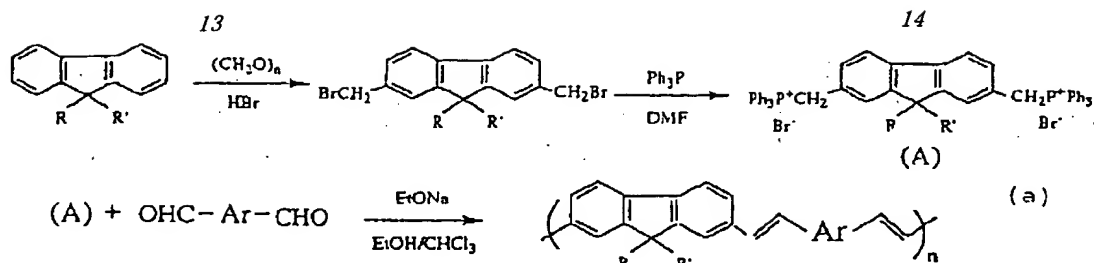
【0012】ここで、本発明の共重合体の重合度は特に限定されないが、有機溶媒への可溶性があつてスピニングやキャスト方法により薄膜が形成し得るという点において、重合度としては1～2, 000が好ましく、3～1, 000であることが更に好ましい。共役二重結合を有する共重合体の製造方法も特に限定されず、例えば、公知の方法であるウィットティヒ (Wittig) 反応 (J. Am. Chem. Soc., 82, p. 4669, Org. React., 25, p. 73 (1977)) (下記の反応式 (a) 参照。式

中、 R 、 R' 、 Ar 及び n は、前記の定義に同じ。反応式 (b) ～ (e) においても同様)、クネベナーゲル (Knoevenagel) 縮合 (J. Org. Chem., 25, p. 813 (1960), Macromolecules, 27, p. 3009 (1994)) (下記の反応式 (b) 参照)、パラジウム触媒によるヘック (Hec k) の方法 (Org. React., 27, p. 345 (1981), Macromolecules, 28, p. 6410 (1995)) (下記の反応式 (c) 参照)、前駆体を用いる方法 (米国特許第3, 401, 152号, J. Chem. Soc., Chem. Commun., p. 32 (1992), Science, 269, p. 376 (1995)) (下記の反応式 (d) 参照)、及びカリウム *tert* ブトキシドのような強塩基を用いた反応 (J. Polym. Sci., Part A-1.4, p. 1337 (1996), Synth. Met., 62, p. 35 (1994)) (下記の反応式 (e) 参照) 等を、本発明に利用することができる。

【0013】

【化7】

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【0014】より詳細に説明すると、ウィッティッヒ反応を利用した共重合体の製造に供する単量体は、一般にホスホニウム塩とジアルデヒドであり、それらをエタノールのような有機溶媒を用い、ナトリウム又はアルカリリチウムのような強塩基性触媒下で反応させるものである。

【0015】本発明においては、ホスホニウム塩として

はビス(プロモ(又はクロロ)メチル)フルオレンやその一部に置換基を有するフルオレン系ホスホニウム塩を、一方、ジアルデヒドとしては、種々のジアルデヒドを用いることができるが、重合後に一般式(1)で表示されるすべてのフルオレン系ホスホニウム塩、及び飽和脂肪族又は芳香族ジアルデヒドが含まれる。具体的には、フルオレン系ホスホニウム塩としては、2,7-ビ

(9)

15

ス (プロモメチル) フルオレンのトリフェニルホスホニウム塩、2, 7-ビス (プロモメチル) -9-アルキルフルオレンのトリフェニルホスホニウム塩のように、フルオレンの9位置の水素1個が、炭素数が22個までのアルキル基、シクロアルキル基、アルコキシ基、アルコキシアルキル基、アルコキシアルコキシアルキル基、アルコキシアルコキシアルコキシアルキル基、炭素数が6~18個のアリール基、アリールオキシ基又はアラルキル基で置換されたフルオレンのホスホニウム塩、及び2, 7-ビス (プロモメチル) -9, 9-ジアルキルフルオレンのトリフェニルホスホニウム塩のようにフルオレンの9位置の水素2個が、それぞれ炭素数が22個までのアルキル基、シクロアルキル基、アルコキシ基、アルコキシアルキル基、アルコキシアルコキシアルキル基、炭素数が6~18個のアリール基、アリールオキシ基又はアラルキル基で置換されたフルオレンのホスホニウム塩が挙げられる。一方、ジアルデヒドとしては、グルタルアルデヒドのような飽和脂肪族ジアルデヒド若しくはフタルアルデヒド、イソフタルアルデヒド、テレフタルアルデヒドのような置換基を有しない芳香族ジアルデヒド若しくは1, 4-ジアルキル-2, 5-ジホルミルベンゼンのように炭素数が22個までのアルキル基、シクロアルキル基、若しくはアルコキシ基又は炭素数6~18個のアリール基、アリールオキシ基、若しくはアラルキル基で芳香環の水素2個が置換された芳香族ジアルデヒド、2, 2'-又は3, 3'-若しくは4, 4'-ジホルミルビフェニル、2, 2'-又は3, 3'-若しくは4, 4'-ジホルミルジフェニルエーテル又はジフェニルスルフィド又はジフェニルアルキルアミンのようなジホルミルビフェニル誘導体、2, 7-ジホルミルフルオレン誘導体、4, 4'-ジホルミルテルフェニルのようなテルフェニルジアルデヒド化合物、1, 8-ジホルミルナフタレンのようなナフタレンジアルデヒド化合物、1, 8-又は3, 6-ジホルミルアントラセンのようなアントラセンジアルデヒド化合物、2, 6-ジホルミルピリジン、2, 5-ジホルミルフラン、2, 5-ジホルミルチオフェン、3, 4-ジアルキル-2, 5-ジホルミルチオフェン、5, 5'-ジホルミル-2, 2'-ビチオフェン、1, 4-ジアルキル-2, 5-ジホルミルピロール、1, 1'-ジアルキル-5, 5'-ジホルミル-2, 2'-ビピロール、5, 5'-ジホルミル-1, 1'-ビピロール、3, 6-ジホルミルジベンゾフラン、3, 6-ジホルミルジベンゾチオフェン、2, 5-ビス (2-又は3-若しくは4-ホルミルフェニル) -1, 3, 4-ジフェニルチアゾール、アルキル-3, 6-ジホルミルカルバゾールのような炭素数が22個までのアルキル基またはシクロアルキル基で置換されたジホルミルカルバゾール等がある。

【0016】また、クネベナーゲル (Knoevenagel) 縮合、

16

を利用した共重合体の製造に供する単量体としては、前記のフルオレン系ホスホニウム塩に代えて、前記のビス (プロモメチル) フルオレン及びその誘導体にシアン化ナトリウムのようなシアン化合物を反応させて製造されたビス (シアノメチル) フルオレン及びその誘導体を用いることができるし、ジアルデヒドとしては、前記のウィッティッヒ (Wittig) 反応で用いたジアルデヒド化合物をそのまま使用することができる。この共重合反応は、二つの単量体化合物をテトラヒドロフラン又はトルエンのような有機溶媒を用い、テトラ-*n*-ブチルアンモニウム水酸化物又はカリウム-*tert*-ブトキシドのような強塩基性触媒下反応させるものである。

【0017】更に、パラジウム触媒によるヘック (Hec k) の方法は、一般に、ジメチルホルムアミドのような塩基性溶媒中で臭素化又はヨウ素化芳香族化合物と芳香族ジビニル化合物を、パラジウムアセテート、トリ-*o*-トリルホスフェン、トリブチルアミンのようなアミン化合物と一緒に用いて縮合反応させるものである。よって、本発明に係る臭素化又はヨウ素化芳香族化合物は、前記のフルオレン及びその誘導体に臭素又はヨウ素を付加して臭素化又はヨウ素化させた誘導体をそのまま使用することができる。例えば、ジメチルホルムアミド又はクロロホルム溶媒中でフルオレン又は9-アルキル若しくは9, 9-ジアルキルフルオレンを臭素で処理すると、2, 7-ジプロモフルオレン又はその9位置の水素がアルキル基で置換されたフルオレン化合物が得られる。一方、芳香族ジビニル化合物としては、例えば、*m*-ジビニルベンゼン、*p*-ジビニルベンゼン、2, 2'-又は3, 3'-若しくは4, 4'-ジビニルビフェニル、2, 5-ジビニルチオフェン、及び2, 6-ジビニルナフタレン等、前記のジアルデヒド化合物をウィッティッヒ反応させて得る。

【0018】更に、前記の前駆体を用いる方法では、単量体として、例えば、本発明に関連してビス (クロロ又はプロモメチル) フルオレン及びその誘導体をメタノール溶媒中でテトラヒドロチオフェンと反応させればテトラヒドロチオフェン塩を容易に得ることができる。よって、前記のウィッティッヒ反応で得られるビス (クロロ又はプロモメチル) フルオレン及びその誘導体をそのまま本発明の単量体の一方として用いることができる。該テトラヒドロチオフェン塩を水又はメタノール溶媒中で重合反応させ、透析した後、真空中で加熱すると本発明の重合体を得られる。

【0019】また、強塩基を用いて重合させる方法では、本発明に係る前記のビス (クロロ又はプロモメチル) フルオレン及びその誘導体をトルエン又はテトラヒドロフラン溶媒中でカリウム-*tert*-ブトキシド又は*n*-ブチルリチウムのような強塩基で反応させると、容易に重合体を得られる。よって、この方法でも前記のビス (クロロ又はプロモメチル) フルオレン及びその誘導体

(10)

17

を単量体としてそのまま使用することができる。

【0020】更に、本発明のフルオレン系高分子を用いるEL素子の構成は、発光層を形成する本発明に係るポリマーを陽極と陰極間に置く、即ち、陽極／発光層／陰極のような一般の素子構成のものに用いることができるし、また公知の事実である正孔注入層及び電子注入層の材料（特開平2-135361号、特開平3-152184号、及び特開平6-207170号）と一緒に用いて構成することもできるため、素子構成については特に限定されない。即ち、陽極／正孔注入層／発光層／電子注入層／陰極という素子構成も本発明のEL素子に包含され、この場合、陽極としては、透明な支持基板としてのガラス、透明プラスチック、又は石英上に電極材料としてのITO、金、銅、酸化スズ、酸化亜鉛のような金属若しくは金属酸化物、又は、ポリピロール、ポリアニリン、ポリチオフェンのような有機半導体化合物が通常10nm-1μの厚さに被覆された材料を用い、一方、陰極としては、ナトリウム、マグネシウム、カルシウム、アルミニウム、インジウム、銀、金、銅のような金属又はそれらの合金を使用することができる。正孔注入層は、ポリビニルカルバゾール、2, 5-ビス(4-ジエチルアミノフェニル)-1, 3, 4-オキサジアゾール、又はN, N'-ジフェニル-N, N'-(3-メチルフェニル)-1, 1'-ビフェニル-4, 4'-ジアミン(TPD)を、電子注入層としてはトリス(8-キノリノール)アルミニウム、2-(4-tert-ブチルフェニル)-5-(4-ビフェニル)-1, 3, 4-オキサジアゾール、2, 4, 7-トリニトロフルオレノンのような公知の化合物をそれぞれ真空蒸着、スパインコーティング、キャストイング、又はLB法等の公知の薄膜形成方法を用い、陽極又は陰極上にこれらの薄膜を形成すればよい。

【0021】そして、本発明の発光重合体を前記の正孔注入層及び電子注入層、又は、本発明の相異なる発光重合体及び可溶性のPPV及びPTH誘導体のような既存の発光重合体と混合して使用することもできる。例えば、ポリビニルカルバゾール及びポリ(1, 4-ヘキシルオキシフェニレン-2, 5-ジイルビニレン)、又はポリ(3-ヘキシルチオフェン)、本発明のフルオレン系高分子をクロロホルムのような有機溶媒に溶かした後、それをスパインコーティング法又はキャストイング法により隣接する層に当該層を形成させることができる。ここで、特に限定されないが、濃度は本発明のフルオレン系高分子をポリビニルカルバゾールに対し0.001重量%以上、好ましくは、0.1~50重量%となるように調製し、薄膜の厚さは5nm~5μ、好ましくは50nm~1μになるようにして使用する。また、正孔伝達層及び電子伝達層以外に一般の有機溶媒に溶解して薄膜形成が可能な高分子も、前記の濃度及び厚さの範囲に混合して使用することができる。例えば、使用可能な高分子

18

としては、ポリメタクリル酸メチル、ポリアクリル酸エステル、ポリスチレン、ポリカーボネート、ポリ塩化ビニル、ポリエチレン、ポリプロピレン、ポリアクリロニトリル、ポリビニルピロリドン、ポリビニルアルコール、ポリ酢酸ビニル、ポリビニルブチラール、ポリビニルアミン、ポリカプロラクトン、ポリエチレンテレフタレート、ポリブテンテレフタレート、ポリウレタン、ABS、ポリスルホン、ポリビニルフッ化物のような熱可塑性プラスチック、又は、ポリアセタール、ポリアミド、ポリイミド、ポリエステル、アルキド樹脂、ウレア樹脂、フラン樹脂、ナイロン、メラミン樹脂、フェノール樹脂、シリコン樹脂、及びエポキシ樹脂のような汎用樹脂等がある。

【0022】

【発明の実施の形態】以下、本発明に係るEL素子用フルオレン系交互共重合体及びそれを用いたEL素子を実施例に基づき詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0023】

【実施例】

単量体合成

本発明に用いられる単量体は重合体が一般式(I)を満足する高分子である限りにおいて、どのような単量体を用いても構わない。また、以下に記載されていないが、一般に容易に合成し得るか、又は公知の化合物、類似化合物、及び購買可能な単量体は、公知の方法及び類似の方法にて合成及び購入して重合体の製造に用いた。

【0024】2, 7-ビス(プロモメチル)-9-ヘキシルフルオレンの合成

30 攪拌機、温度計、及び還流コンデンサーを備えた1Lの3口フラスコに9-ヘキシルフルオレン50: 0g(0.2mol)、パラホルムアルデヒド60g(2.0mol)、及び30%のHBr硝酸溶液500gを入れ、60℃の温度で24時間反応させた。反応後、常温まで温度を低下させ、薄黄色の固体を析出させた。これを濾過した後、水とメタノールとで数回洗浄し、40℃の真空オーブン中で十分に乾燥させ、74g(85%収率)の白色の固体を得た。融点は143~145℃であった。1H-NMRスペクトル(溶媒CDCl₃), δ0.88(t, 3H, CH₃), 1.25(m, 8H, CH₂), 2.01(m, 2H, CH₂), 3.98(t, 1H, C

【0025】2, 7-ビス(プロモメチル)-9-ヘキシルフルオレンのトリフェニルホスホニウム塩の合成

40 攪拌機、温度計、及び還流コンデンサーを備えた1Lの3口フラスコに2, 7-ビス(プロモメチル)-9-ヘキシルフルオレン43.6g(0.1mol)、トリフェニルホスフィン78.7g(0.3mol)、及びN, N-ジメチルホルムアミド500mLを入れ、還流温度で12時間反応させた。反応後、常温まで温度を低下させ、次いで攪拌された3Lのエチルエーテル溶媒中に徐々に滴下

(11)

19

し、白色の固体を析出させた。これを濾過した後、エチルエーテルで数回洗浄し、40℃の真空オーブン中で十分に乾燥させ、92.2g(96%収率)の白色の固体を得た。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.25(br, 3H, CH₃), 1.60-1.24(m, 10H, CH₂), 2.83(t, 1H, CH), 5.66-5.76(d, 4H, CH₂Br), 6.76-7.11(m, 6H, フルオレニル芳香族), 7.49-7.81(m, 30H, 芳香族)

【0026】2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレンの合成

攪拌機、温度計、及び還流コンデンサーを備えた1Lの3口フラスコに9, 9-ジヘキシルフルオレン33.4g(0.1mol)、パラホルムアルデヒド30g(1.0mol)、30%のHBr硝酸溶液300g、及び48%のHBr水溶液120gを入れ、60℃で24時間反応させた。反応後、常温まで温度を低下させ、500mLの冷水で該反応生成物を希釈した後、200mLのジクロロメタンにて3回抽出した。該抽出された有機溶液を合わせた後、再び水、飽和NaHCO₃水溶液及び塩水で洗った。その後、得られた有機溶液を無水硫酸マグネシウムにて乾燥し、濾過後、溶媒を蒸発させ、粘性のある液体を得た。該液体をシリカゲルカラム(酢酸エチル/ヘキサン=1/10の混合溶液)を用いて精製し溶媒を蒸発させ、44.2g(85%収率)の無色透明な粘性のある液体を得た。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.59(br, 6H, CH₃), 0.72-1.04(m, 16H, CH₂), 1.95(m, 4H, CH₂), 4.60(s, 4H, CH₂Br), 7.33-7.62(m, 6H, 芳香族)

【0027】2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレンのトリフェニルホスホニウム塩の合成

攪拌機、温度計、及び還流コンデンサーを備えた1Lの3口フラスコに2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレン26.0g(0.05mol)、トリフェニルホスフィン39.3g(0.15mol)、及びN, N-ジメチルホルムアミド300mLを入れ、還流温度で12時間反応させた。反応後、常温まで温度を低下させ、次いで攪拌された1.5Lのエチルエーテル溶媒中に徐々に滴下し、白色の固体を析出させた。これを濾過した後、エチルエーテルで数回洗浄し、40℃の真空オーブン中で十分に乾燥させ、49.6g(95%収率)の白色の固体を得た。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.11(br, 6H, CH₃), 0.62-1.09(m, 16H, CH₂), 1.39(m, 4H, CH₂), 5.21-5.28(d, 4H, CH₂Br), 6.83-7.27(m, 6H, フルオレニル芳香族), 7.54-7.75(m, 30H, 芳香族)

【0028】2, 7-ビス(シアノメチル)-9-ヘキシルフルオレンの合成

窒素雰囲気下で攪拌機、温度計、及び還流コンデンサーを備えた500mLの3口フラスコに精製したジメチルス

20

ルホキシド300mLとシアン化ナトリウム2.8g

(0.057mol)を入れ、90℃に加熱しながら攪拌した。その後、シアン化物が完全に溶解したら加熱を止め、2, 7-ビス(プロモメチル)-9-ヘキシルフルオレン10g(0.023mol)を徐々に添加した後、90℃で12時間反応させた。この場合、該反応液の色は赤い色から段々濃い暗茶色に変化する。反応終了後、温度を常温まで低下させ、500mLの蒸留水を加えた後、200mLのジクロロメタンで3回該反応物を抽出し、該抽出物に有機溶媒を混合した後、無水硫酸マグネシウムを用いて十分に乾燥させる。該溶液を濾過した後、溶媒を蒸発させ、オレンジ色の固体を得た。これを酢酸エチル/ヘキサン(1:1)中で再結晶させ、5.7g(76%の収率)の固体を得た。その融点は130~131℃であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.89(t, 3H, CH₃), 1.25(m, 8H, CH₂), 2.04(m, 2H, CH₂), 3.90(s, 4H, CH₂CN), 4.02(t, 1H, CH), 7.35-7.79(m, 6H, 芳香族)

【0029】2, 7-ジプロモ-9, 9-ジヘキシルフルオレンの合成

窒素雰囲気下で攪拌機付の500mLの3口フラスコにて9, 9-ジヘキシルフルオレン33.4g(0.1mol)を精製したN, N-ジメチルホルムアミド300mLに完全に溶かした後、臭素48g(0.3mol)を徐々に添加した。次いで、常温で12時間反応させた後、500mLの水に注ぎ200mLのジエチルエーテルで3回抽出し、有機溶媒と混合した後、チオ硫酸ナトリウム水溶液及び塩水で連続的に洗い、有機物層を分離し、無水硫酸マグネシウムを用いて十分に乾燥させた。該溶液を濾過した後、溶媒を蒸発させ、薄黄色の固体を得た。これをヘキサン中で再結晶させ、43.8g(89%収率)の白色の結晶固体を得た。その融点は61~62℃であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.55(br, s, 6H, CH₃), 0.73-1.03(m, 16H, CH₂), 1.90-1.94(m, 4H, CH₂), 7.41-7.53(m, 6H, 芳香族)

【0030】2, 7-ビス(プロモメチル)-9-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}フルオレンの合成

攪拌機、温度計、及び還流コンデンサーを備えた1Lの3口フラスコに9-メトキシエトキシエチルフルオレン31.2g(0.1mol)、パラホルムアルデヒド30g(1.0mol)、30%のHBr硝酸溶液300g、及び48%のHBr水溶液120gを入れ、60℃で24時間反応させた。反応後、常温まで温度を低下させ、500mLの冷水で反応物を希釈した後、200mLのジクロロメタンで3回抽出した。該抽出された有機溶液を混合した後、再び水、飽和NaHCO₃水溶液及び塩水で連続して洗い、有機物層を分離し、無水硫酸マグネシウムを用いて十分に乾燥させた。該溶液を濾過した後、溶媒を蒸発させ、薄黄色の粘性のある液体を得た。該液

(12)

21

体をシリカゲルカラム（酢酸エチル／ヘキサン＝1／4の混合溶液）を用いて精製し溶媒を蒸発させ、39.8 g（80%収率）の無色透明な粘性のある液体を得た。1H-NMRスペクトル（溶媒CDCl₃）， δ 2.28(m, 3H, OC H₃), 3.41-3.71(m, 12H, OCH₂CH₂), 4.09(t, 1H, CH), 4.60(s, 4H, CH₂Br), 7.25-7.71(m, 6H, 芳香族)

【0031】2, 7-ビス（プロモメチル）-9-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕フルオレンのトリフェニルホスホニウム塩の合成

攪拌機、温度計、及び還流コンデンサーを備えた1Lの3口フラスコに2, 7-ビス（プロモメチル）-9-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕フルオレン24.9 g（0.05mol）、トリフェニルホスフィン39.3 g（0.15mol）、及びN, N-ジメチルホルムアミド300mLを入れ、還流温度で12時間反応させた。反応後、常温まで温度を低下させ、攪拌された1.5Lのエチルエーテル溶媒中に徐々に滴下し、白色の固体を析出させ、それを濾過した後、エチルエーテルで数回洗浄し、40℃の真空オーブン中で十分に乾燥させ、48.5 g（95%収率）の白色の固体を得た。

1H-NMRスペクトル（溶媒CDCl₃）， δ 1.22-1.41(m, 2H, CH₂), 2.16-2.42(br, s, 3H, OCH₃), 3.41-3.71(m, 10H, OCH₂CH₂), 4.18(t, 1H, CH), 5.58-5.81(d, 4H, CH₂Br), 6.81-7.22(m, 6H, フルオレン芳香族), 7.27-7.84(m, 30H, 芳香族)

【0032】N-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕-3, 6-ジホルミルカルバゾールの合成

窒素雰囲気下で攪拌機、温度計、及び還流コンデンサーを備えた1Lの3口フラスコにジメチルホルムアルデヒド191 g（2.61mol）及び1, 2-ジクロロエタン100mLを入れ、0℃まで十分に冷却した後、これに塩化ホスホリル（Phosphorus Oxychloride）197.6 g（1.29mol）を徐々に滴下した。次いで、該反応液を常温まで昇温して、1時間攪拌した後、再び0℃まで冷却し、これに1, 2-ジクロロエタン30mLに希釈されたN-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕カルバゾール21.0 g（0.067mol）を徐々に添加した。1時間後反応温度を90℃まで昇温し、24時間反応させた後、再び常温まで温度を低下させ、1.5Lの氷水にて希釈した後、200mLのジクロロメタンにて3回抽出した。該抽出された有機溶液を混合した後、再び水、飽和NaHCO₃水溶液及び塩水で連続して洗い、有機物層を分離し、無水硫酸マグネシウムを用いて十分に乾燥させた。該溶液を濾過した後、溶媒を蒸発させ、黄色の粘性のある液体を得た。該液体を少量の酢酸エチル中で3回再結晶させ、融点が108～109℃である11.1 g（45%収率）の薄黄色の固体を得た。

22

1H-NMRスペクトル（溶媒CDCl₃）， δ 3.48-3.56(m, 11H, OCH₂CH₂及びOCH₃), 3.98(t, 2H, OCH₂), 4.61(t, 2H, NCH₂), 7.62(d, 2H, 芳香族), 8.13(d, 2H, 芳香族), 8.68(s, 2H, 芳香族), 10.15(s, 2H, CHO)

【0033】重合体の合成

実施例1

ポリ（フルオレン-2, 7-ジイルビニレン-N-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕カルバゾール-3, 6-ジイルビニレン）の合成

窒素雰囲気下で攪拌機付の100mLフラスコに2, 7-ビス（プロモメチル）フルオレンのトリフェニルホスホニウム塩1.75 g（2mmol）とN-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕-3, 6-ジホルミルカルバゾール0.74 g（2mmol）とを入れ、無水エタノール60mL及びクロロホルム20mLに完全に溶かした後、これに無水エタノールに金属ナトリウムが5%溶解された溶液2.3 gを注射器で取って徐々に滴下する。次いで、常温で12時間反応させた後、0.1N塩酸水溶液1mLを入れて反応を終了し、析出した固体を濾過した。該固体をメタノールで洗い40℃の真空オーブン中で十分に乾燥させ、0.82 gの黄色固体の標題重合体を得た。該重合体をテトラヒドロフランを溶媒としポリスチレンを基準物質として用いてGPCにより重量平均分子量及び分子量分布を測定した結果は、それぞれ2, 700及び1.69であった。

1H-NMRスペクトル（溶媒CDCl₃）， δ 3.3-4.0(br, d, フルオレン-CH₂及びカルバゾール-アルコキシ), 4.3-4.6(br, s, NCH₂), 6.5-8.4(br, m, ビニル、及び芳香族)

【0034】実施例2

ポリ（9-ヘキシルフルオレン-2, 7-ジイルビニレン-N-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕カルバゾール-3, 6-ジイルビニレン）の合成

実施例1と同様な方法により、2, 7-ビス（プロモメチル）-9-ヘキシルフルオレンのトリフェニルホスホニウム塩1.92 g（2mmol）とN-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕-3, 6-ジホルミルカルバゾール0.74 g（2mmol）とを重合させた結果、0.86 gの黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ5, 900及び1.87であった。

1H-NMRスペクトル（溶媒CDCl₃）， δ 0.6-2.2(br, m, フルオレン-脂肪族), 3.4-4.0(br, d, フルオレン-CH, フルオレン, カルバゾール及びアルコキシ), 4.3-4.6(br, s, NCH₂), 6.6-8.3(br, m, ビニル、及び芳香族)

【0035】実施例3

ポリ（9, 9-ジヘキシルフルオレン-2, 7-ジイルビニレン-N-〔2-〔2-（2-メトキシエトキシ）エトキシ〕エチル〕カルバゾール-3, 6-ジイルビニレン）の合成

50

(13)

23

ン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09 g (2 mmol)とN-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}-3, 6-ジホルミルカルバゾール0.74 g (2 mmol)とを重合させた結果、0.92 gの黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ11, 400及び2, 004であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.6-2.2(br, m, フルオレン-脂肪族), 3.3-3.9(br, d, カルバゾール-アルコキシ), 4.3-4.6(br, s, NCH₂), 6.6-8.4(br, m, ビニル、及び芳香族)

【0036】実施例4

ポリ(9-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}-フルオレン-2, 7-ジイルビニレン-N-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}カルバゾール-3, 6-ジイルビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}フルオレンのトリフェニルホスホニウム塩2.05 g (2 mmol)とN-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}-3, 6-ジホルミルカルバゾール0.74 g (2 mmol)とを重合させた結果、0.81 gの黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ2, 900及び1, 411であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 2.1-2.4(br, s, フルオレン-CH₂), 3.2-3.9(br, m, フルオレン-CH, フルオレンとカルバゾール-アルコキシ), 4.3-4.6(br, s, NCH₂), 6.5-8.4(br, m, ビニル、及び芳香族)

【0037】実施例5

ポリ(9-ヘキシルフルオレン-2, 7-ジイル-1-シアノビニレン-N-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}カルバゾール-3, 6-ジイル-1-シアノビニレン)の合成

窒素雰囲気下で攪拌機付の100 mLフラスコにて2, 7-ビス(シアノメチル)-9-ヘキシルフルオレン0.66 g (2 mmol)とN-{2-[2-(2-メトキシエトキシ)エトキシ]エチル}-3, 6-ジホルミルカルバゾール0.74 g (2 mmol)とを精製したテトラヒドロフラン20 mLに完全に溶かした後、-7.8℃まで冷却した。これに1.0 molの水酸化テトラ-n-ブチルアンモニウムを含有するメタノール0.04 mLをマイクロ注射器で滴下した。次いで、30分後、温度を50℃まで徐々に昇温させて12時間反応させ、0.1 N塩酸水溶液1 mLを入れて反応を終了させた後、該反応液を25

24

0 mLのメタノールに徐々に注いで固体を析出させた。該固体をメタノールで洗い40℃の真空オーブン中で十分に乾燥させ、0.80 gの黄色固体の標題重合体を得た。該固体をテトラヒドロフランを溶媒としポリスチレンを基準物質として用いてGPCにより重量平均分子量及び分子量分布を測定した結果は、それぞれ38, 700及び4, 28であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.5-2.1(br, m, フルオレン-脂肪族), 3.2-4.0(br, m, フルオレン-CH, 及びフルオレンとカルバゾール-アルコキシ), 4.3-4.6(br, s, NCH₂), 6.5-8.2(br, m, ビニル、及び芳香族)

【0038】実施例6

ポリ(9, 9-ジヘキシルフルオレン-2, 7-ジイルビニレン-m-フェニレンビニレン)の合成

窒素雰囲気下で攪拌機付の100 mLフラスコにて2, 7-ジブromo-9, 9-ジヘキシルフルオレン0.98 g (2 mmol)、m-ジビニルベンゼン0.26 g (2 mmol)、酢酸パラジウム18.2 mg、及びトリ-n-ブチルホスフィン12.4 mgを精製したジメチルホルムアミド15 mLに完全に溶かした後、トリブチルアミン1.4 mLを注射器で滴下した。次いで、30分後、温度を100℃まで徐々に昇温させて24時間反応させ、0.1 N塩酸水溶液1 mLを入れて反応を終了させた後、該反応液250 mLのメタノールに徐々に注いで固体を析出させた。該固体をメタノールで洗い40℃の真空オーブン中で十分に乾燥させ、0.81 gの黄色固体の標題重合体を得た。該重合体をテトラヒドロフランを溶媒としポリスチレンを基準物質として用いてGPCにより重量平均分子量及び分子量分布を測定した結果は、それぞれ35, 400及び3, 21であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.4-2.2(br, m, 脂肪族), 6.5-7.8(br, m, ビニル、及び芳香族)

【0039】実施例7

ポリ(9, 9-ジヘキシルフルオレン-2, 7-ジイルビニレン-p-フェニレンビニレン)の合成

実施例6と同様な方法により、2, 7-ジブromo-9, 9-ジヘキシルフルオレン0.98 g (2 mmol)とp-ジビニルベンゼン0.26 g (2 mmol)とを重合させた結果、0.85 gの黄色固体の標題重合体を得た。実施例6と同様な方法により、重量平均分子量及び分子量分布を測定した結果は、それぞれ26, 300及び2, 89であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.5-2.2(br, m, 脂肪族), 6.5-7.8(br, m, ビニル、及び芳香族)

【0040】実施例8

ポリ(9-ヘキシルフルオレン-2, 7-ジイルビニレン-p-フェニレンビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9-ヘキシルフルオレンのトリフェニルホスホニウム塩1.92 g (2 mmol)とテレフタルアルデヒド

(14)

25

0.27 g (2 mmol) とを重合させた結果、0.62 g の黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ7,200及び3.41であった。

¹H-NMRスペクトル (溶媒CDCl₃), δ 0.7-2.1(br, m, 脂肪族), 3.7-4.0(br, s, フルオレン-CH), 6.5-7.8(br, m, ビニル、及び芳香族)

【0041】実施例9

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイルビニレン-p-フェニレンビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09 g (2 mmol) とテレフタルアルデヒド0.27 g (2 mmol) とを重合させた結果、0.68 g の黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ38,200及び4.45であった。

¹H-NMRスペクトル (溶媒CDCl₃), δ 0.5-2.2(br, m, 脂肪族), 6.5-7.8(br, m, ビニル、及び芳香族)

【0042】実施例10

ポリ(9-ヘキシルフルオレン-2,7-ジイルビニレン-m-フェニレンビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9-ヘキシルフルオレンのトリフェニルホスホニウム塩1.92 g (2 mmol) とイソフタルアルデヒド0.27 g (2 mmol) とを重合させた結果、0.64 g の薄黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ12,700及び5.01であった。

¹H-NMRスペクトル (溶媒CDCl₃), δ 0.6-2.2(br, m, 脂肪族), 3.6-4.0(br, s, フルオレン-CH), 6.4-7.8(br, m, ビニル、及び芳香族)

【0043】実施例11

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイルビニレン-m-フェニレンビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09 g (2 mmol) とイソフタルアルデヒド0.27 g (2 mmol) とを重合させた結果、0.69 g の薄黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ43,500及び4.12であった。

¹H-NMRスペクトル (溶媒CDCl₃), δ 0.4-2.2(br, m, 脂肪族), 6.5-7.8(br, m, ビニル、及び芳香族)

【0044】実施例12

ポリ(9-ヘキシルフルオレン-2,7-ジイルビニレ

26

ン-ピリジン-2,6-ジイルビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9-ヘキシルフルオレンのトリフェニルホスホニウム塩1.92 g (2 mmol) と2,6-ジホルミルピリジン0.27 g (2 mmol) とを重合させた結果、0.66 g の黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ20,800及び5.10であった。

¹H-NMRスペクトル (溶媒CDCl₃), δ 0.7-2.2(br, m, 脂肪族), 3.7-3.9(br, s, フルオレン-CH), 6.6-7.8(br, m, ビニル、及び芳香族)

【0045】実施例13

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイルビニレン-ピリジン-2,6-ジイルビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09 g (2 mmol) と2,6-ジホルミルピリジン0.27 g (2 mmol) とを重合させた結果、0.68 g の黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ35,700及び3.33であった。

¹H-NMRスペクトル (溶媒CDCl₃), δ 0.4-2.2(br, m, 脂肪族), 6.6-7.8(br, m, ビニル、及び芳香族)

【0046】実施例14

ポリ(9-ヘキシルフルオレン-2,7-ジイルビニレン-2,2'-ビピロール-5,5'-ジイルビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9-ヘキシルフルオレンのトリフェニルホスホニウム塩1.92 g (2 mmol) と5,5'-ジホルミル-2,2'-ビピロール0.40 g (2 mmol) とを重合させた結果、0.78 g の黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ3,500及び1.75であった。

¹H-NMRスペクトル (溶媒CDCl₃), δ 0.7-2.0(br, m, 脂肪族), 3.6-3.8(br, s, フルオレン-CH), 5.4-5.8(br, d, ピロール-CH₂), 6.0-7.8(br, m, ビニル、及び芳香族)

【0047】実施例15

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイルビニレン-2,2'-ビピロール-5,5'-ジイルビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09 g (2 mmol) と5,5'-ジホルミル-2,2'-ビピロール0.40 g (2 mmol) とを重合させた結果、0.85 g の黄色固体の標題重合体

(15)

27

を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ8,100及び2,03であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.4-2.1(br, m, 脂肪族), 5.5-5.8(br, d, ピロール-CH₂), 6.1-7.8(br, m, ビニル、及び芳香族)

【0048】実施例16

ポリ(9-ヘキシルフルオレン-2, 7-ジイルビニレン-フラン-2, 5-ジイルビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9-ヘキシルフルオレンのトリフェニルホスホニウム塩1.92g(2mmol)と2, 5-ジホルミルフラン0.25g(2mmol)とを重合させた結果、0.62gの褐色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ20, 200及び4.35であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.6-2.2(br, m, 脂肪族), 3.8-4.0(br, s, フルオレン-CH), 6.2-7.8(br, m, ビニル、及び芳香族)

【0049】実施例17

ポリ(9, 9-ジヘキシルフルオレン-2, 7-ジイルビニレン-フラン-2, 5-ジイルビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と2, 5-ジホルミルフラン0.25g(2mmol)とを重合させた結果、0.58gの濃黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ9, 600及び1.78であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.5-2.1(br, m, 脂肪族), 6.2-7.8(br, m, ビニル、及び芳香族)

【0050】実施例18

ポリ(9-ヘキシルフルオレン-2, 7-ジイルビニレン-チオフェン-2, 5-ジイルビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9-ヘキシルフルオレンのトリフェニルホスホニウム塩1.92g(2mmol)と2, 5-ジホルミルチオフェン0.28g(2mmol)とを重合させた結果、0.62gの濃褐色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ9, 300及び3.89であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.6-2.2(br, m, 脂肪族), 3.7-4.0(br, s, フルオレン-CH), 6.4-7.8(br, m, ビニル、及び芳香族)

【0051】実施例19

ポリ(9, 9-ジヘキシルフルオレン-2, 7-ジイルビニレン-チオフェン-2, 5-ジイルビニレン)の合

28

成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と2, 5-ジホルミルチオフェン0.28g(2mmol)とを重合させた結果、0.68gの濃黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ5, 600及び1.73であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.3-2.1(br, m, 脂肪族), 6.4-7.7(br, m, ビニル、及び芳香族)

【0052】実施例20

ポリ(フルオレン-2, 7-ジイルビニレン-3-ヘキシルチオフェン-2, 5-ジイルビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)フルオレンのトリフェニルホスホニウム塩1.75g(2mmol)と3-ヘキシル-2, 5-ジホルミルチオフェン0.45g(2mmol)とを重合させた結果、0.58gの赤色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ8, 600及び3.43であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.8-1.8(br, m, 脂肪族), 2.4-2.7(br, s, チオフェン-CH₂), 3.7-4.0(br, s, フルオレン-CH₂), 6.4-7.8(br, m, ビニル、及び芳香族)

【0053】実施例21

ポリ(9, 9-ジヘキシルフルオレン-2, 7-ジイルビニレン-3-ヘキシルチオフェン-2, 5-ジイルビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と3-ヘキシル-2, 5-ジホルミルチオフェン0.45g(2mmol)とを重合させた結果、0.64gの赤色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ8, 200及び1.95であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.6-3.0(br, m, 脂肪族), 6.5-7.8(br, m, ビニル、及び芳香族)

【0054】実施例22

ポリ(9, 9-ジヘキシルフルオレン-2, 7-ジイルビニレン-2, 2'-ビチオフェン-5, 5'-ジイルビニレン)の合成

実施例1と同様な方法により、2, 7-ビス(プロモメチル)-9, 9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と5, 5'-ジホルミル-2, 2'-ビチオフェン0.44g(2mmol)とを重合させた結果、0.62gの濃赤色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の

(16)

29

重量平均分子量及び分子量分布を測定した結果は、それぞれ14,600及び2,52であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.6-2.2(br, m, 脂肪族), 6.6-7.8(br, m, ビニル、及び芳香族)

【0055】実施例23

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイル
ビニレン-1,4-ジヘキソキシ-2,5-フェニレン
ビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と1,4-ジヘキソキシ-2,5-ジホルミルベンゼン0.66g(2mmol)とを重合させた結果、0.98gの褐色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ13,500及び3.05であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.4-2.2(br, m, 脂肪族), 4.0-4.3(br, s, OCH₂), 6.7-7.8(br, m, ビニル、及び芳香族)

【0056】実施例24

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイル
ビニレン-ジフェニルエーテル-2,2'-ジイルビ
ニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と2,2'-ジホルミルジフェニルエーテル0.45g(2mmol)とを重合させた結果、0.68gの薄黄色固体の標題の重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ18,500及び3.52であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.5-2.1(br, m, 脂肪族), 6.7-7.9(br, m, ビニル、及び芳香族)

【0057】実施例25

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイル
ビニレン-(3-メトキシ)-1,4-フェニレン-
1,6-ジオキシヘキサメチレン-(2-メトキシ)-
1,4-フェニレンビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と{[2,2'-ジメトキシ(4,4'-ジホルミル)]-1,6-フェノキシ}ヘキサノ.77g(2mmol)とを重合させた結果、1.08gの薄緑色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ8,200及び2.51であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.3-2.1(br, m, 脂肪族), 3.6-4.2(br, m, OCH₂), 6.4-7.7(br, m, ビニル、及び芳香族)

30

【0058】実施例26

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイル
ビニレン-1,2-フェニレン-1,6-ジオキシヘキ
サメチレン-1,2-フェニレンビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と、[(2,2'-ジホルミル)-1,6-ジフェノキシ]ヘキサノ.65g(2mmol)とを重合させた結果、0.85gのアンズ色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ4,500及び1.79であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.4-2.0(br, m, 脂肪族), 3.9-4.1(br, s, OCH₂), 6.6-7.7(br, m, ビニル、及び芳香族)

【0059】実施例27

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイル
ビニレン-1,3-フェニレン-1,6-ジオキシメチ
レン-1,3-フェニレンビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と、[(3,3'-ジホルミル)-1,6-ジフェノキシ]ヘキサノ.65g(2mmol)とを重合させた結果、0.88gの薄黄色固体の標題の重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ9,800及び2.23であった。

¹H-NMRスペクトル(溶媒CDCl₃), δ 0.4-2.0(br, m, 脂肪族), 3.9-4.1(br, s, OCH₂), 6.5-7.7(br, m, ビニル、及び芳香族)

【0060】実施例28

ポリ(9,9-ジヘキシルフルオレン-2,7-ジイル
ビニレン-1,4-フェニレン-1,6-ジオキシヘキ
サメチレン-1,4-フェニレンビニレン)の合成

実施例1と同様な方法により、2,7-ビス(プロモメチル)-9,9-ジヘキシルフルオレンのトリフェニルホスホニウム塩2.09g(2mmol)と、[(3,3'-ジホルミル)-1,6-ジフェノキシ]ヘキサノ.65g(2mmol)とを重合させた結果、0.86gの黄色固体の標題重合体を得た。実施例1と同様な方法により、該重合体の重量平均分子量及び分子量分布を測定した結果は、それぞれ6,800及び1.68であった。¹H-NMRスペクトル(溶媒CDCl₃), δ 0.4-2.1(br, m, 脂肪族), 3.8-4.1(br, s, OCH₂), 6.6-7.7(br, m, ビニル、及び芳香族)

【0061】以上の実施例で製造された重合体の構造をそれぞれ表1に示すと共に、実施例11で製造された高分子のプロトン及び炭素-13核磁気共鳴スペクトルそ

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(17)

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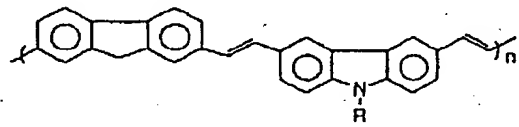
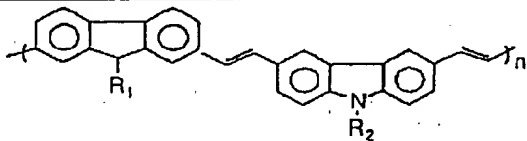
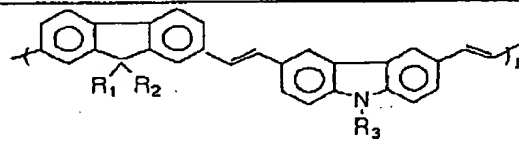
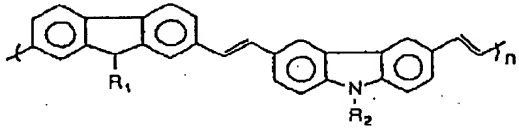
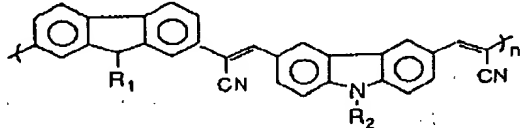
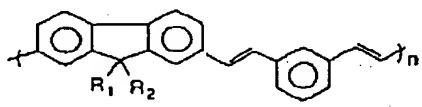
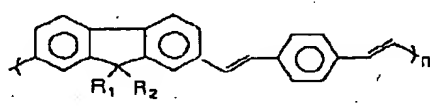
れぞれ図1及び図2に示す。

*【表1】

【0062】

*

表1 重合体の化学構造

実施例	構 造 式	備 考
1		R = 2 - [2 - (2 - メトキシ エトキシ) エトキシ] エチル
2		R ₁ = ヘキシル R ₂ = 2 - [2 - (2 - メトキシ シエトキシ) エトキシ] エチル
3		R ₁ = R ₂ = ヘキシル R ₃ = 2 - [2 - (2 - メトキシ シエトキシ) エトキシ] エチル
4		R ₁ = R ₂ = 2 - [2 - (2 - メトキシエト キシ) エトキシ] エチル
5		R ₁ = ヘキシル R ₂ = 2 - [2 - (2 - メトキシ シエトキシ) エトキシ] エチル
6		R ₁ = R ₂ = ヘキシル
7		R ₁ = R ₂ = ヘキシル

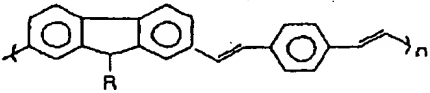
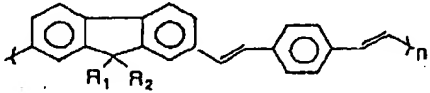
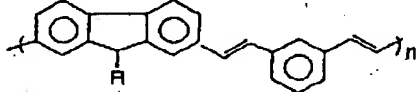
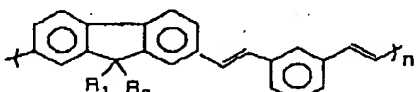
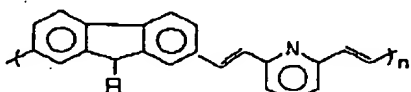
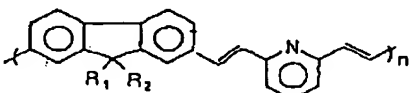
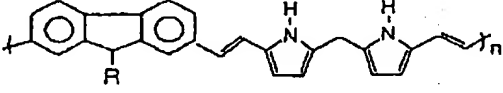
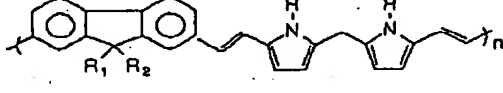
【0063】

【表2】

(18)

33

34

実施例	構 造 式	備 考
8		R = ヘキシル
9		R ₁ = R ₂ = ヘキシル
10		R = ヘキシル
11		R ₁ = R ₂ = ヘキシル
12		R = ヘキシル
13		R ₁ = R ₂ = ヘキシル
14		R = ヘキシル
15		R ₁ = R ₂ = ヘキシル

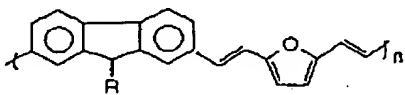
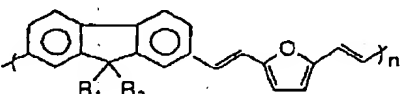
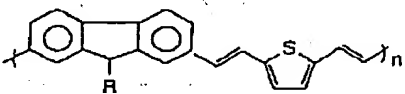
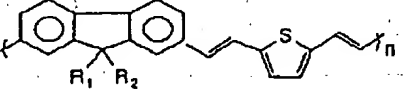
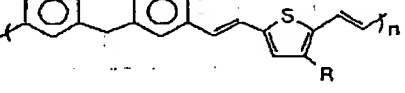
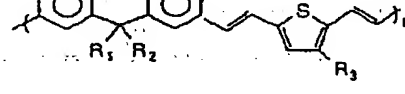
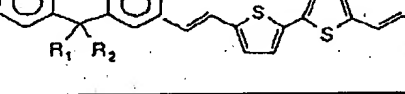
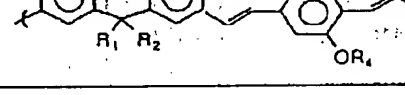
【0064】

【表3】

(19)

35

36

実施例	構 造 式	備 考
16		R = ヘキシル
17		R ₁ = R ₂ = ヘキシル
18		R = ヘキシル
19		R ₁ = R ₂ = ヘキシル
20		R = ヘキシル
21		R ₁ = R ₂ = R ₃ = ヘキシル
22		R ₁ = R ₂ = ヘキシル
23		R ₁ = R ₂ = R ₃ = R ₄ = ヘキシル

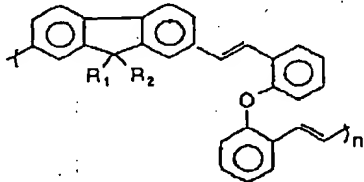
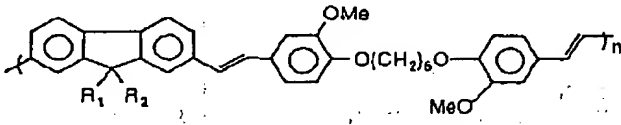
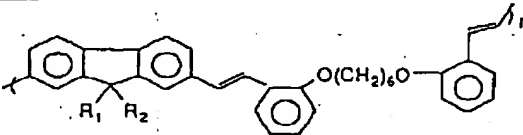
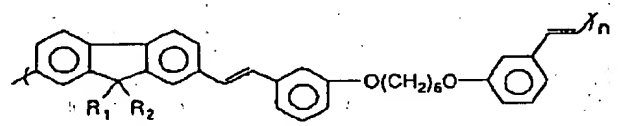
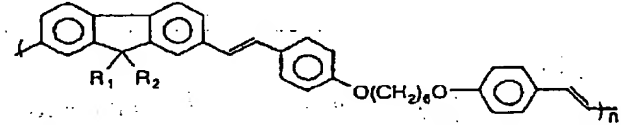
【0065】

【表4】

(20)

37

38

実施例	構 造 式	備 考
24		$R_1 = R_2 = \text{ヘキシル}$
25		$R_1 = R_2 = \text{ヘキシル}$
26		$R_1 = R_2 = \text{ヘキシル}$
27		$R_1 = R_2 = \text{ヘキシル}$
28		$R_1 = R_2 = \text{ヘキシル}$

【0066】紫外線、光発光及び電界発光特性と、EL素子の製造

前記の実施例で製造された重合体を用いて紫外線 (Ultraviolet、以下、UVと称する) スペクトルと光発光 (Photoluminescence、以下、PLと称する) スペクトルを薄膜のフィルムから求めた。ここで、薄膜の形成は、前記重合体0.1gを5mLのクロロホルム溶液に溶解させ、0.2μmのフィルタを用いて精製した後、薄膜の厚

さが100nm程度になるようにスピン速度を制御 (通常900~1,200rpm)したスピンコーティング法によった。コーティング終了後の試料を常温で乾燥させた後、まず、UVスペクトルを求め、その後、UVピーク極大値の波長を用いてPLスペクトルを求めた。このようにして得られた結果を表2に要約して表示した。

【0067】

【表5】

表2 実施例で製造された重合体の特性

実施例	UV (λ_{\max} nm)	PL (λ_{\max} nm)	T _{deg} * (°C)
1	406	470, 492	212.1
2	408	470	216.5
3	408	466	216.8
5	420	558, 496	314.9
6	382	428, 448	414.4
7	412	480	420.1
8	406	490, 564	414.0
10	368	453	405.7
12	386	551	411.8
13	388	495, 530	421.8
14	392	466	378.2
15	398	467	403.8
23	444	509, 547	383.1
24	368	425, 445	410.4
25	388	458	397.8
26	374	429, 449	408.9
27	380	420, 441	416.9
28	386	447	410.0

* T_{deg} は熱重量分析による重合体の分析開始温度。

【0068】表2に示すように、本発明の重合体は広い領域のPLピーク極大値(420～564nm)を示す。即ち、本発明の重合体は多様な色相の光発光をするものである。尚、これらのUVスペクトルとPLスペクトルを図3～図23に示す。

【0069】次に、一般に用いられる素子構成、即ちITO基板/発光層/電極からなるEL素子を製造してEL特性を調査した。ここで、発光層は、前記の実施例で製造された重合体をそのまま使用するか、又は前述した汎用高分子、例えば、ポリビニルカルバゾール、ポリメチルメタアクリレート、ポリスチレン、及びエポキシ樹脂をクロロホルム溶媒で本発明に係る重合体と混合したものをを用い、電極としてはアルミニウムを選択した。

【0070】EL素子の製造は、前記のUVスペクトル及びPLスペクトル測定用試料の製造と同様に、ITOガラス基板上に厚みが100nmとなるようにスピニング法にて発光層を形成し、次いで該発光層上にアルミニウムを真空蒸着させることによった。このように構成されたEL素子の電圧-電流特性を求めるため、電圧を-10Vから25V又はそれ以上まで変化させながら電流変化を測定した。図24～図31に示すように、本発明に係る重合体の臨界電圧、即ち、それ以上の電圧で電界発光が行われるということを示す電圧は10～20Vであった。また、電圧-電界発光特性を図32～図35に示す。電界発光した光を分析するため、ITOガラス面を透過する光のスペクトルを分光器で測定し、最大発光を示す波長から発光色相を定義した。更に、ELスペクトルを図36～図39に、前記の実施例中製造さ

れた複数の重合体と前記の汎用高分子とを混合した発光体のPLスペクトルと、該発光体を前記の構成に従って作成したEL素子の電圧-電流特性と電圧-電界発光特性及びELスペクトルを、それぞれ図40～図46、図47～図50、図51～図52にそれぞれ示した。更に、本発明で用いた素子構成の概要図を図53に示した。

【0071】

【発明の効果】以上説明したように本発明に係るEL素子用フルオレン系交互共重合体及びそれを用いた電界発光素子は、その製造方法が簡単で、最終物質の構造が明確であり、有機溶媒によく溶解され得る多様な種類の高分子EL材料を製造し得るという効果がある。

【図面の簡単な説明】

【図1】本発明の実施例11に係る重合体¹H-NMRスペクトルを示した図である。

【図2】本発明の実施例11に係る重合体¹³C-NMRスペクトルを示した図である。

【図3】本発明の実施例1に係る重合体のUVスペクトル(実線。以下、同様)及びPLスペクトル(破線。以下、同様)を示した図である。

【図4】本発明の実施例2に係る重合体のUVスペクトル及びPLスペクトルを示した図である。

【図5】本発明の実施例3に係る重合体のUVスペクトル及びPLスペクトルを示した図である。

【図6】本発明の実施例5に係る重合体のUVスペクトル及びPLスペクトルを示した図である。

【図7】本発明の実施例6に係る重合体のUVスペクトル及びPLスペクトルを示した図である。

【図 3 2】本発明の実施例 6 に係る重合体を用いた E L 素子の電圧－電界発光特性を示した図である。

【図50】本発明の実施例13に係る重合体（重量分率0.5）とポリビニルカルバゾールとの混合物フィルムを用いたE1素子の電圧－電界発光特性を示した図であ

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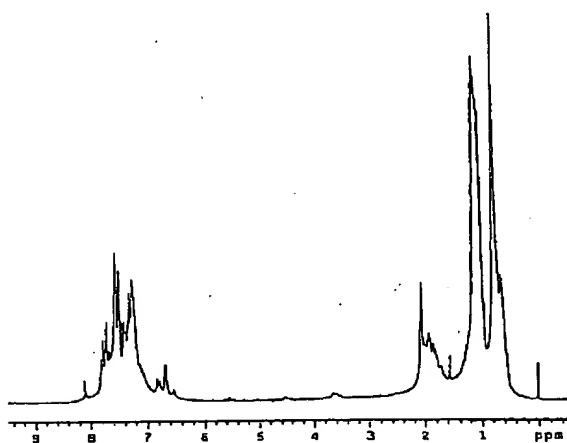
43

る。

【図51】本発明の実施例6に係る重合体（重量分率0.2）とポリビニルカルバゾールとの混合物フィルムを用いたEL素子のELスペクトルを示した図である。

【図52】本発明の実施例7に係る重合体（重量分率

【図1】

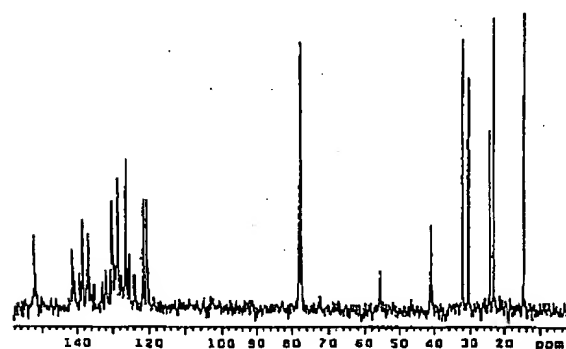


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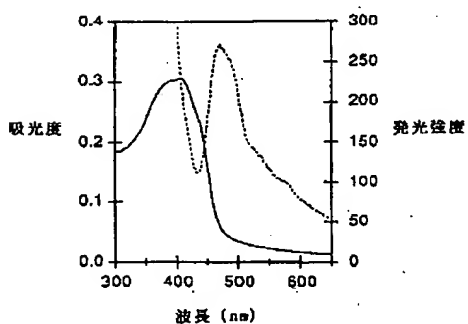
0.2）とポリビニルカルバゾールとの混合物フィルムを用いたEL素子のELスペクトルを示した図である。

【図53】本発明に係るフルオレン系交互共重合体、又はこれと汎用高分子との混合物フィルムを発光層として用いたEL素子の構成例を示した図である。

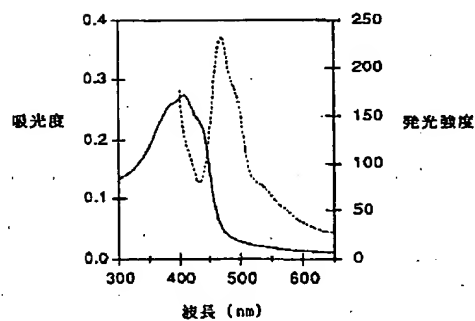
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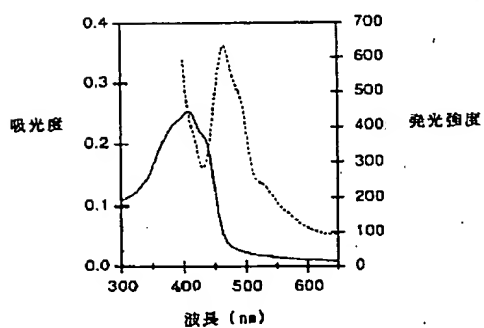
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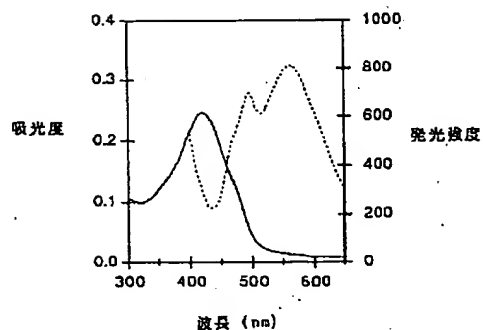
【図4】



【図5】

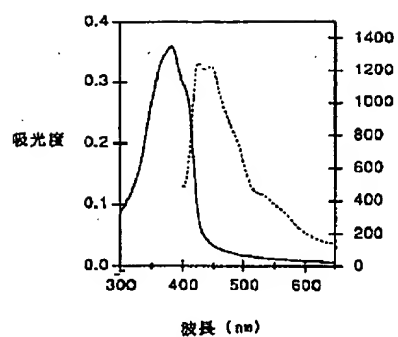


【図6】

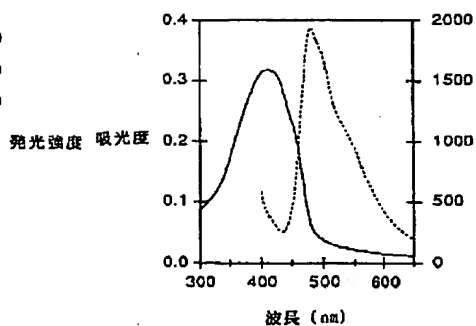


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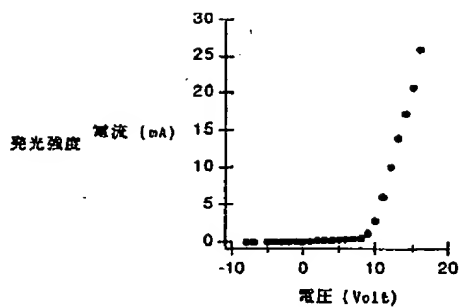
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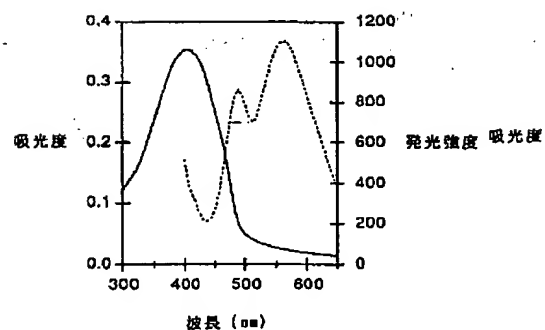
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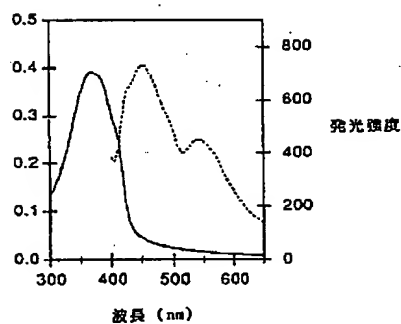
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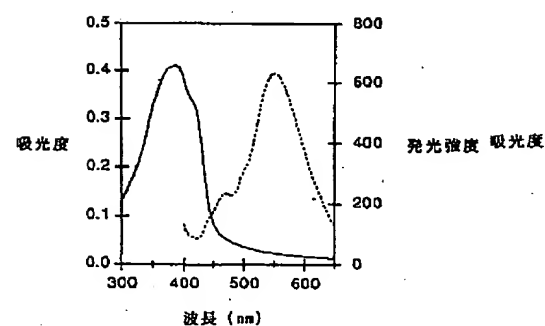
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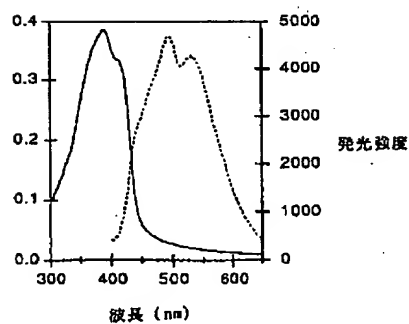
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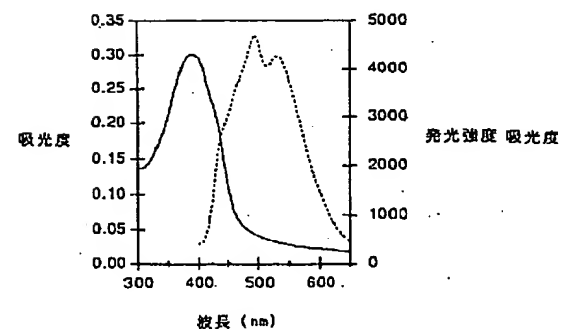
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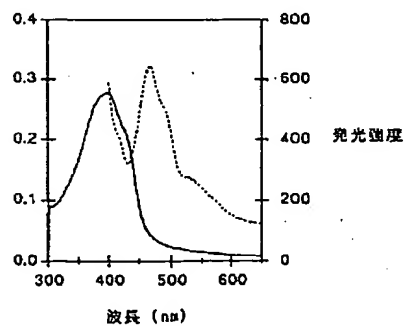
【図12】



【図13】

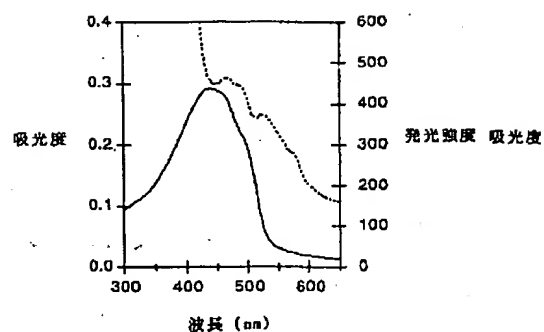


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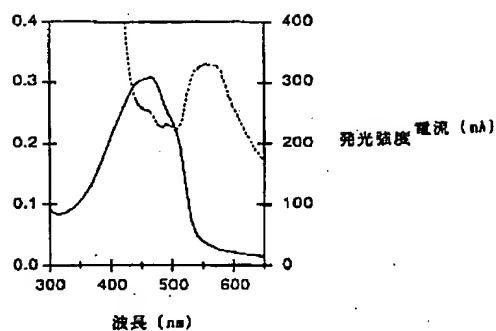


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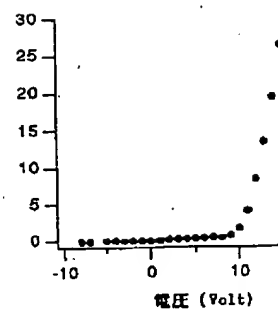
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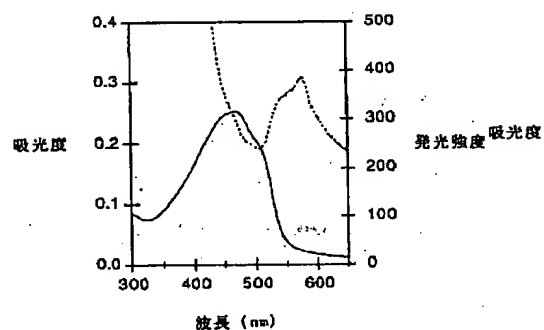
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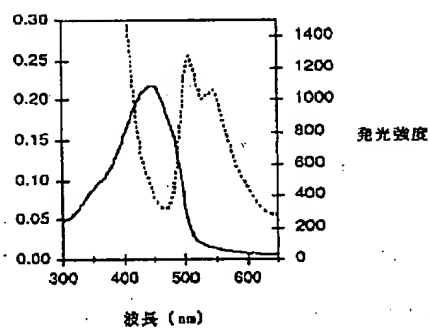
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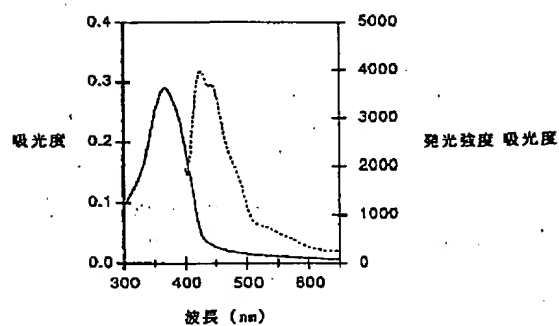
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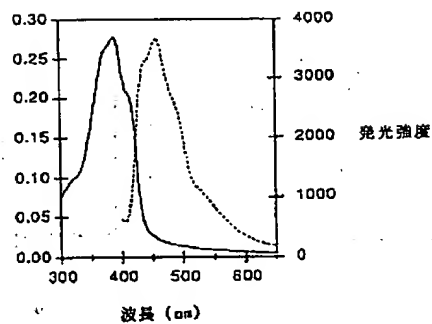
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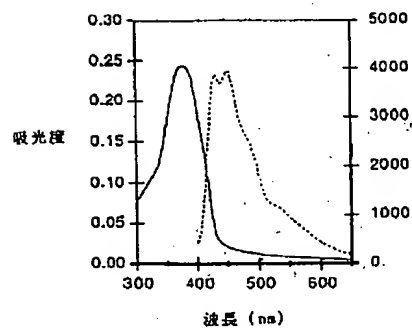
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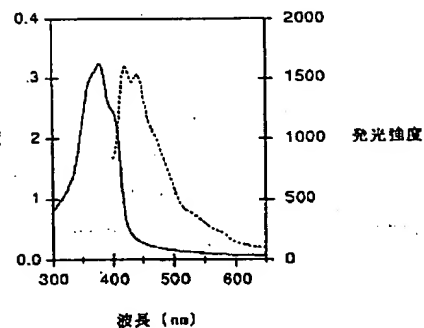
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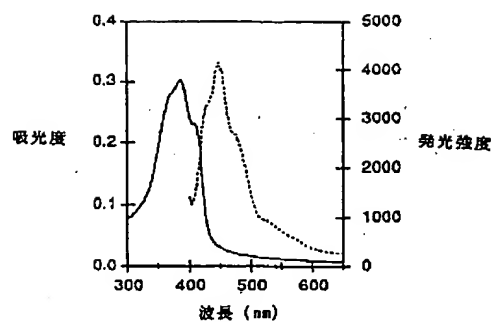


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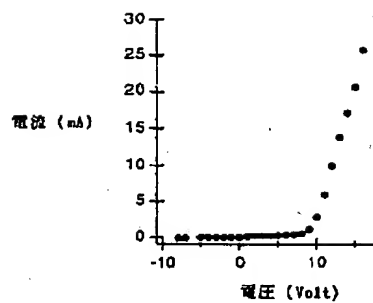


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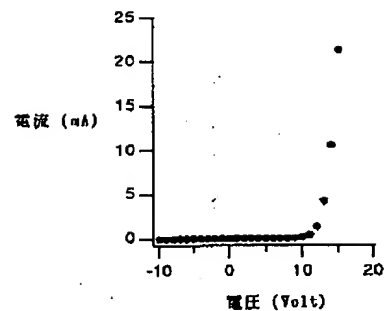
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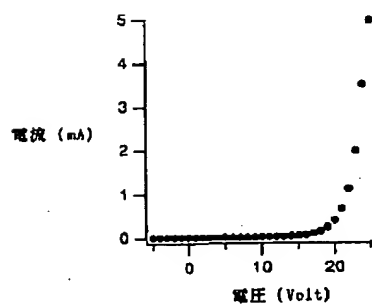
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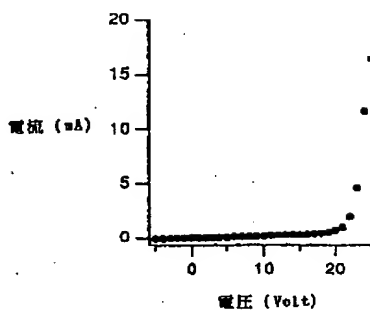
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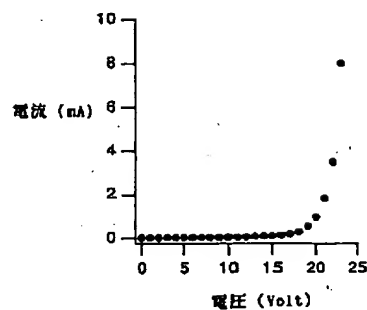
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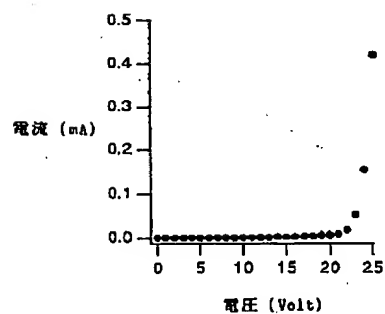
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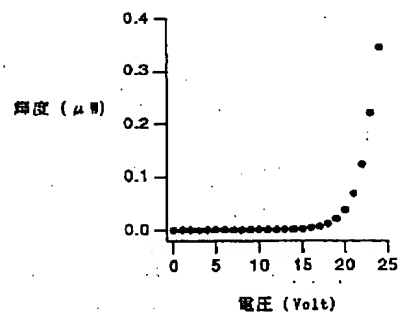
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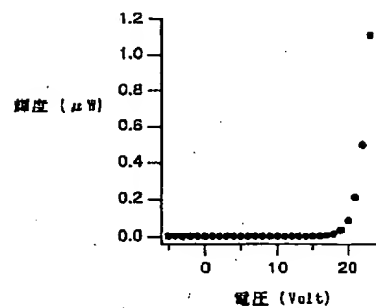
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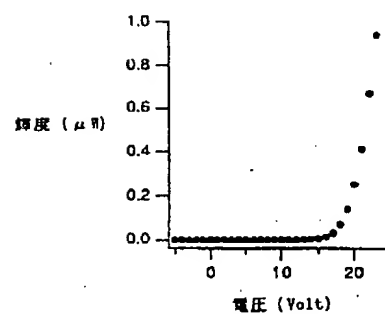
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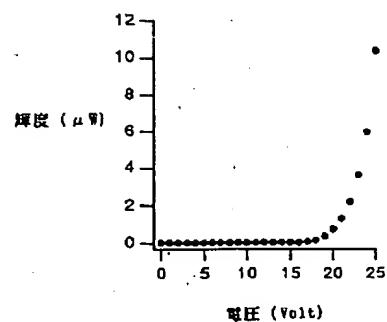
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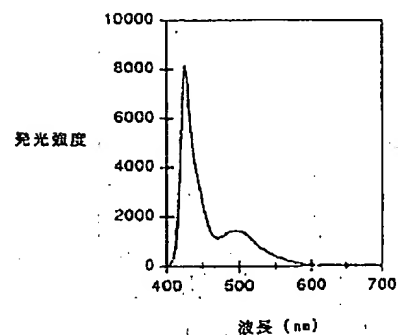
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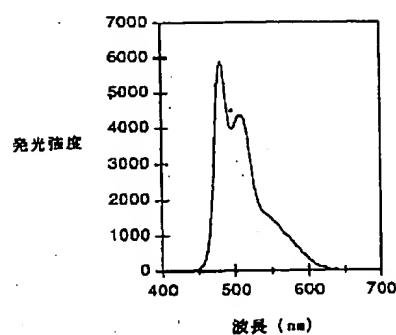


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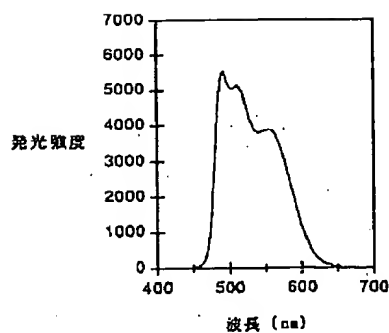


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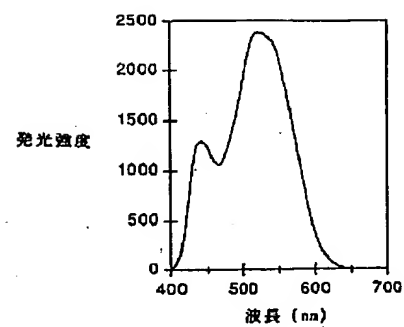
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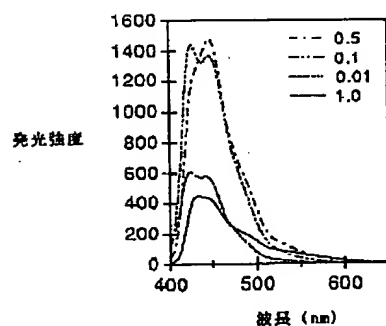
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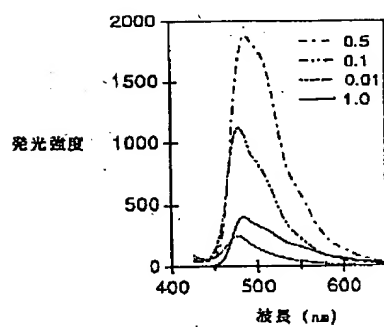
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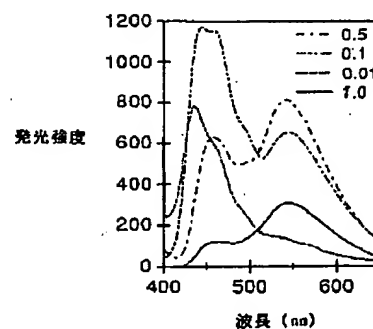
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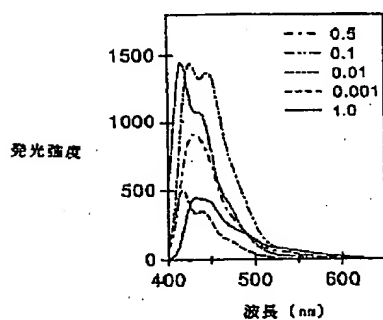
【図 4 1】



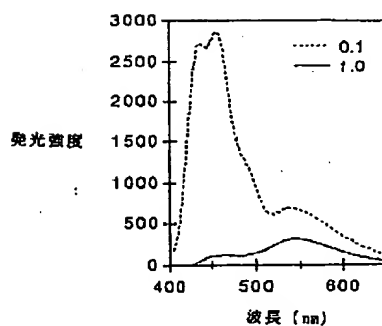
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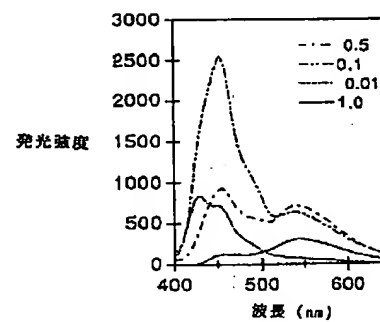
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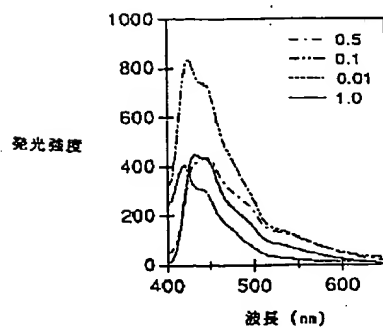
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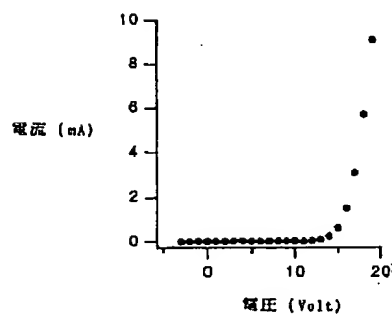
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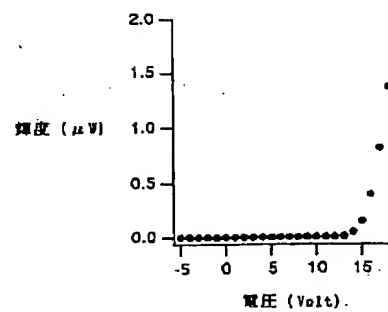
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【図 4 7】

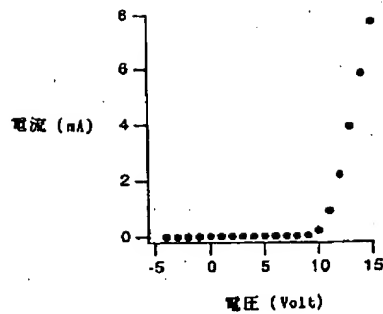


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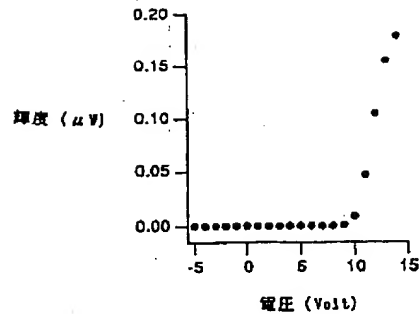


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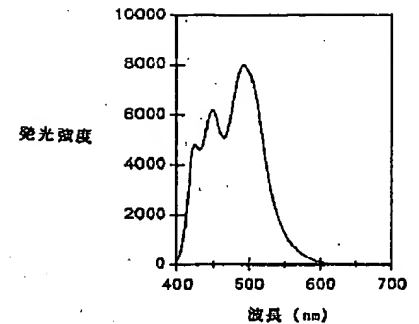
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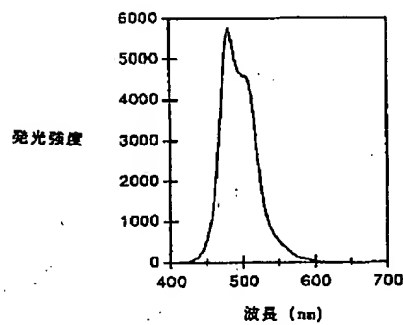
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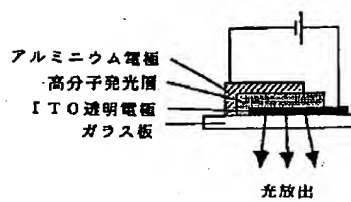
【図51】



【図52】



【図53】



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RI JUNEI
KIN ZAIKEI

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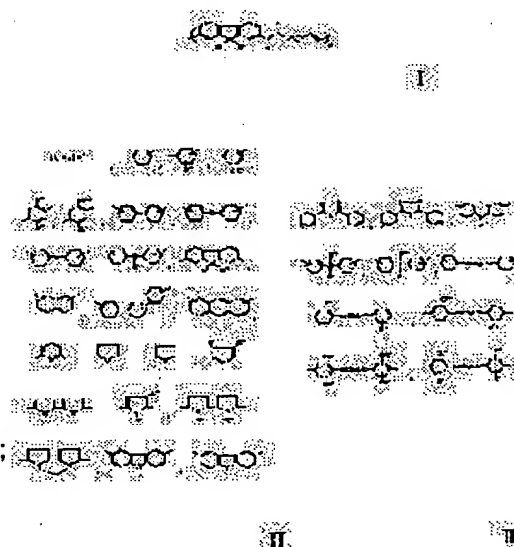
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(54) FLUORENE POLYMER FOR EL ELEMENT AND EL ELEMENT USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a fluorescent material of a polymer-based EL element, which is produced by a simple process, has a well-defined structure of a final substance and is highly soluble in organic solvents by using a specified alternating fluorene copolymer.

SOLUTION: This material is an alternating fluorene copolymer represented by formula I (wherein R and R' are each H, a 22C or lower alkyl, a cycloalkyl, an alkoxy, an alkoxyalkyl, an alkoxyalkoxyalkyl, an alkoxyalkoxyalkoxyalkyl, a 6-18C aryl, an alkylthio or an aralkyl; X is H or cyano; Ar is a group of formula II or a group of formula III; R'' and R''' are each the same as R or R'; n' is 1-22; and n is 1-2,000). This copolymer or a mixture thereof with a general-purpose polymeric material is used as a luminescent material of an EL element.



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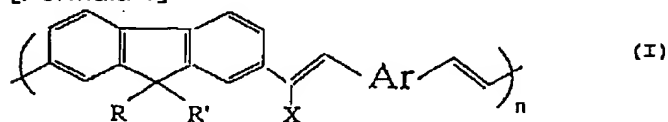
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CLAIMS

[Claim(s)]

[Claim 1] General formula (I)

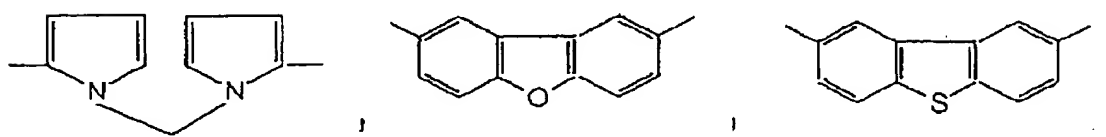
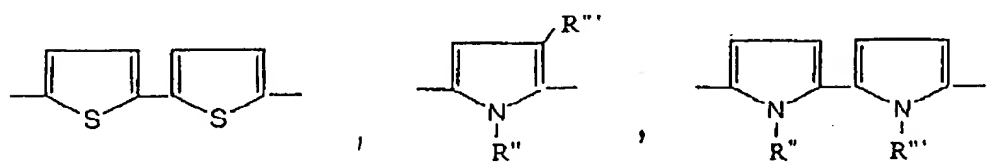
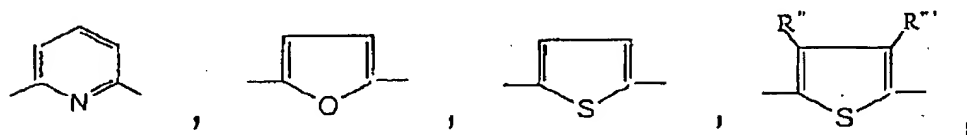
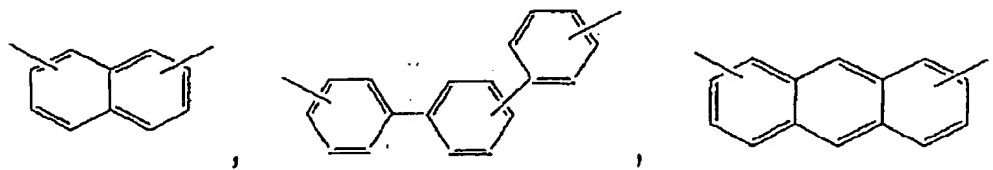
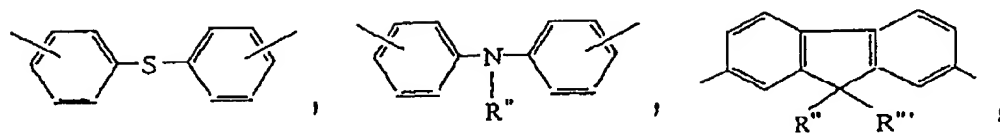
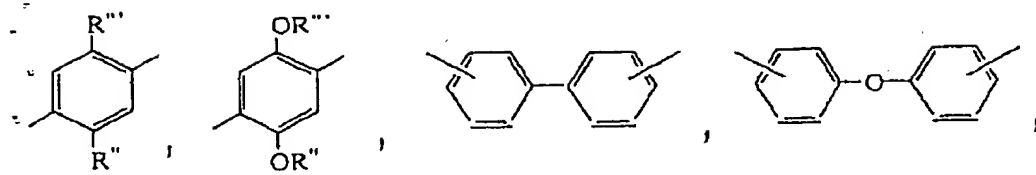
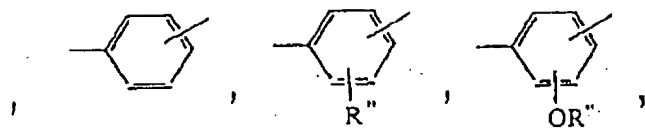
[Formula 1]



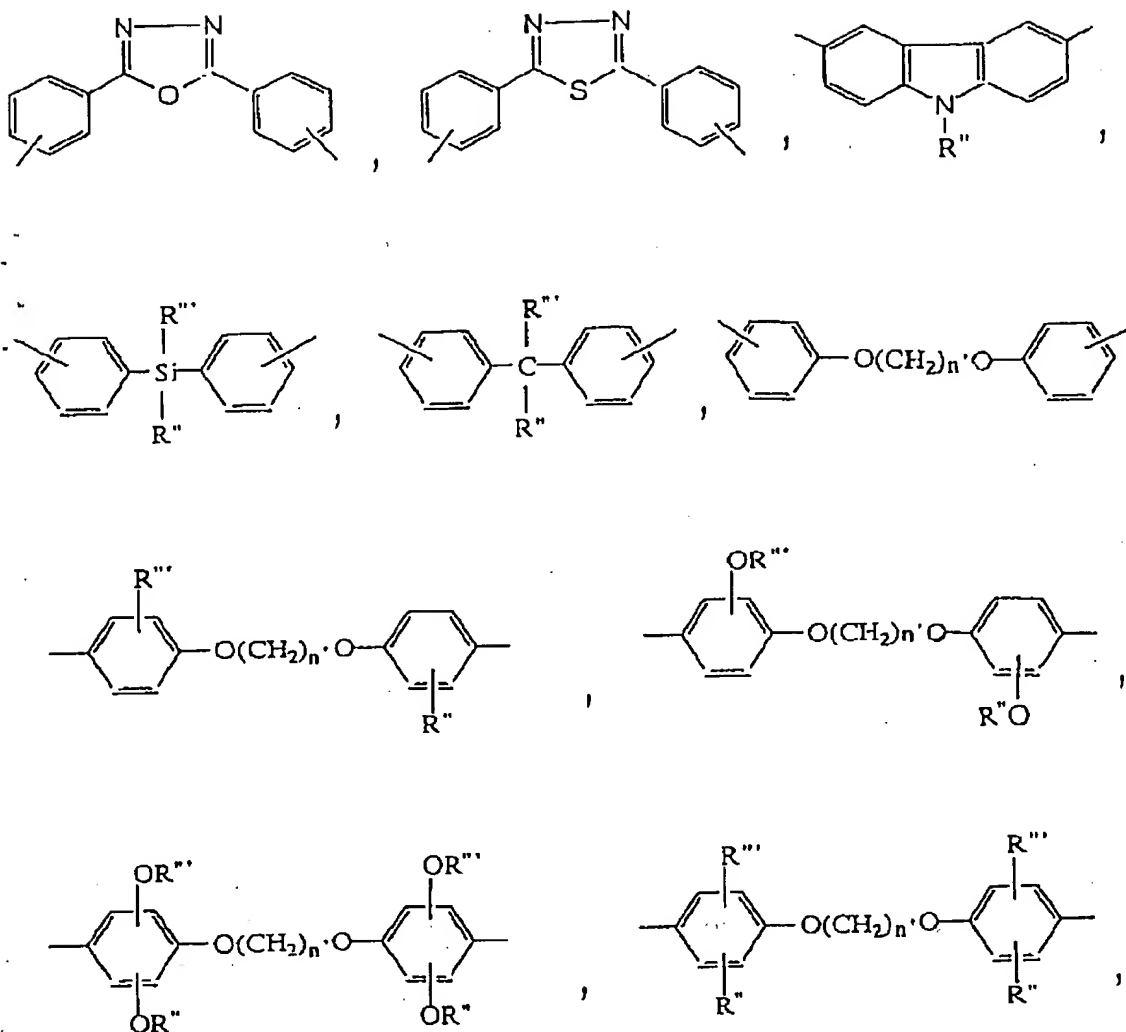
(For hydrogen and a carbon number, among a formula, R and R' expresses the aryl group they are [aryl group] 6-18 pieces, an aryloxy group, or an aralkyl radical, X expresses hydrogen or a cyano group, respectively, and Ar is [the alkyl group to 22 pieces, a cycloalkyl radical, an alkoxy group, an alkoxyalkyl group, an alkoxy alkoxyalkyl group, an alkoxy alkoxy alkoxyalkyl group, and a carbon number] a formula (II).)

[Formula 2]

- (CH₂)_{n'} -



[Formula 3]



the radical shown by (' expresses R'' and the aryl group whose number is 6-18, an aryloxy group, or an aralkyl radical, respectively, and a carbon number expresses [the alkyl group to 22 pieces, a cycloalkyl radical, an alkoxy group, an alkoxyalkyl group, an alkoxy alkoxyalkyl group an alkoxy alkoxy alkoxyalkyl group, and a carbon number] R'' of integers to 1-22 among a formula, as for n) — expressing — n — the integer of 1-2,000 — expressing — the fluorene system alternating copolymer shown.

[Claim 2] The EL element which contains a fluorene system alternating copolymer according to claim 1 as a luminescent material of a luminous layer.

[Claim 3] The EL element according to claim 2 whose aforementioned luminescent material is the mixture of the aforementioned fluorene system alternating copolymer and general-purpose polymeric materials.

[Claim 4] The EL element according to claim 3 as which the aforementioned general-purpose polymeric materials are chosen from a polyvinyl carbazole, a PORIMECHIRU meta-acrylic rate, polystyrene, or an epoxy resin.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the EL element using the fluorene system alternating copolymer (FluorenebasedAlternating Copolymers) and it which are used as a luminescent material of the electroluminescence (EL is called Electroluminescence and the following) component of a macromolecule system.

[0002]

[Description of the Prior Art] These days, the EL element currently studied is the semi-conductor of an inorganic system like GaAs, and this semi-conductor has small magnitude, and since it is a low power, it is used now as the display of small area, a light emitting diode (LED is called Light Emitting Diode and the following) lamp, and semiconductor laser. However, there is demerit in which the process of high clarification is required, it is difficult to manufacture LED of a large area, and it also difficult to obtain efficient blue glow in manufacture of such a component. In addition, although there is an inorganic system EL element which made the macromolecule distribute the inorganic semi-conductor and this by which the fluorescent substance ion of metallic compounds was added, they have high driver voltage, and in order that they may operate by high electric field, a trouble is in the stability of a semi-conductor.

[0003] Then, the organic system which solved such a trouble recently (Appl.Phys.Lett, 51, and p.913 (1987)) And a macromolecule system (Nature, 347, and p.539) EL (1990) ingredient is developed, and research to this field is done briskly. That is, if an electrical potential difference is applied to the EL element which placed the macromolecule (the international patent WO 92/No. 03491, WO 93/No. 14177, and WO 94/No. 15368) which vapor-deposits organic dye, or (JP,6-13360,A and JP,7-26254,A) has conjugated double bond between an anode plate and cathode, generally, from an anode plate side, from a cathode side, an electron is poured in for an electron hole, respectively, and when they move and recombine with a luminous layer, light will be emitted. And research to which it is going to apply these to the next-generation monotonous color display which substitutes for a current cathode-rays tube (CRT), a plasma display (PDP), and a liquid crystal display (LCD) or an electrochemical cel, image sensors, and an optical coupler is done.

[0004]

[Problem(s) to be Solved by the Invention] However, although extent which the component which vapor-deposited and manufactured the aforementioned organic dye has a problem in manufacturing repeatability and a uniform thin film, and has such a problem with a macromolecule system component is solved, commercializing has many technical problems which should still be solved in stability, effectiveness, and the point of a life. On the other hand as the aforementioned giant-molecule system luminescent material, polyphenylene vinylene (PPV is called hereafter), the poly thiophene (PTh is called hereafter), and a polyphenylene system macromolecule (Synth.Met, 50 (1-3), p.491 (1992) and Adv.Mater., 4, p.36 (1992)) etc. — it is — current, although research to such polymeric materials is done There is a problem that it cannot dissolve in an organic solvent. furthermore, PPV which a suitable substituent is introduced, and workability is raised and carries out luminescence of blue, green, and a color with various red and a PTh derivative (Synth.Met., 62, and p.35 (1994) —) Although Adv.Mater., 4,

p.36 (1994) and Macromolecules, 28, and p.7525 (1995) are proposed, the production process is complicated and a problem is in stability.

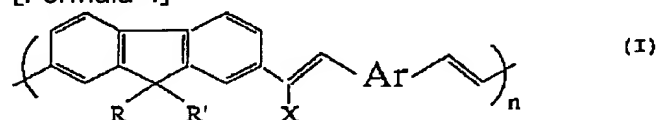
[0005] Moreover, the fluorene system macromolecule which carries out blue luminescence is also proposed (Jpn.I.Appl.Phys., 30, and p.1941 (1991)). This was also using the matter which cannot manufacture the macromolecule which has various conjugated double bond, and its manufacture approach. Then, this invention persons came to complete this invention, as a result of repeating research, in order to manufacture the macromolecule EL ingredient of the varieties which the manufacture approach is easy, and the structure of the last matter is clear, and may be well dissolved in an organic solvent.

[0006]

[Means for Solving the Problem] The fluorene system alternating copolymer used as a luminescent material of the macromolecule system EL element concerning this invention is displayed by the following general formula (I).

[0007]

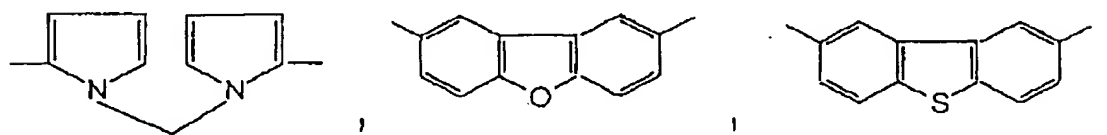
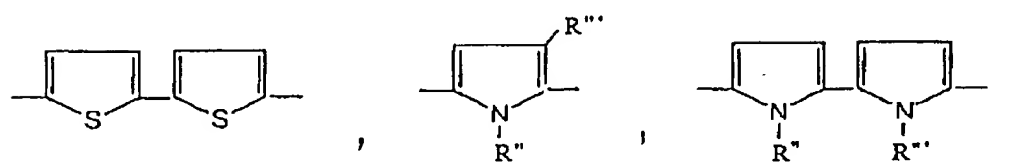
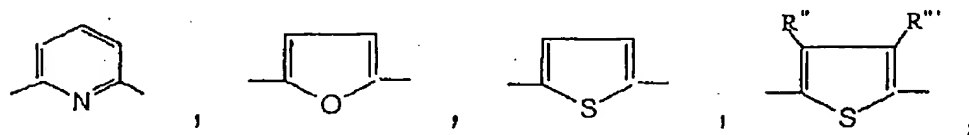
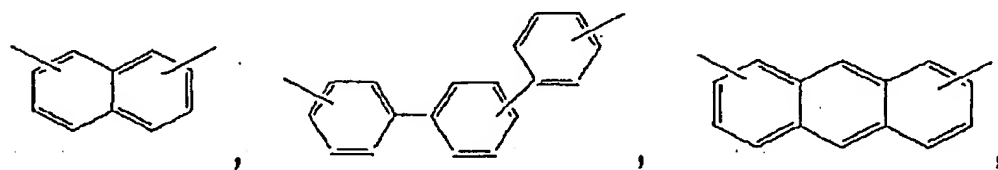
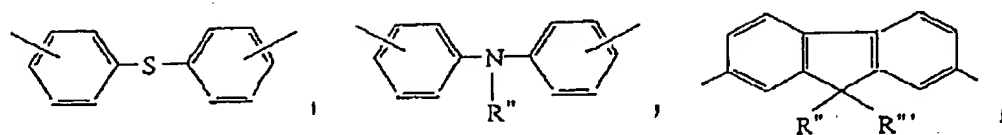
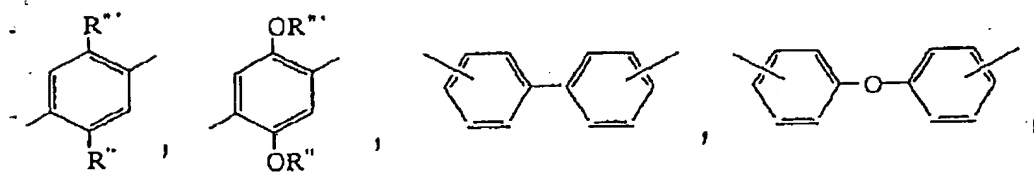
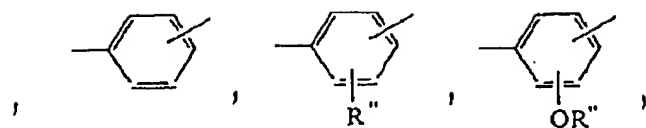
[Formula 4]



[0008] inside of formula, R, and R' — respectively — hydrogen and a carbon number — the alkyl group to 22 pieces — A cycloalkyl radical, an alkoxy group, an alkoxyalkyl group, an alkoxy alkoxyalkyl group, An alkoxy alkoxy alkoxyalkyl group, the aryl group whose carbon number is 6–18 pieces, An aryloxy group or an aralkyl radical is expressed. For example, methyl, ethyl, Propyl, isopropyl, butyl, isobutyl, pentyl, hexyl, Ethylhexyl one, heptyl, octyl, iso octyl, nonyl, DESHIRU, Dodecyl, hexadecyl, octadecyl, DOKODESHIRU, cyclo propyl, Cyclopentyl, cyclohexyl, methoxy, ethoxy **, butoxy, Hexyloxy one, methoxy ethoxyethyl, methoxyethoxy ethoxyethyl, phenyl, phenoxy, tolyl, benzyl, naphthyl, anthryl, etc. are expressed, X expresses hydrogen or a cyano group, and Ar is the following formula [0009].

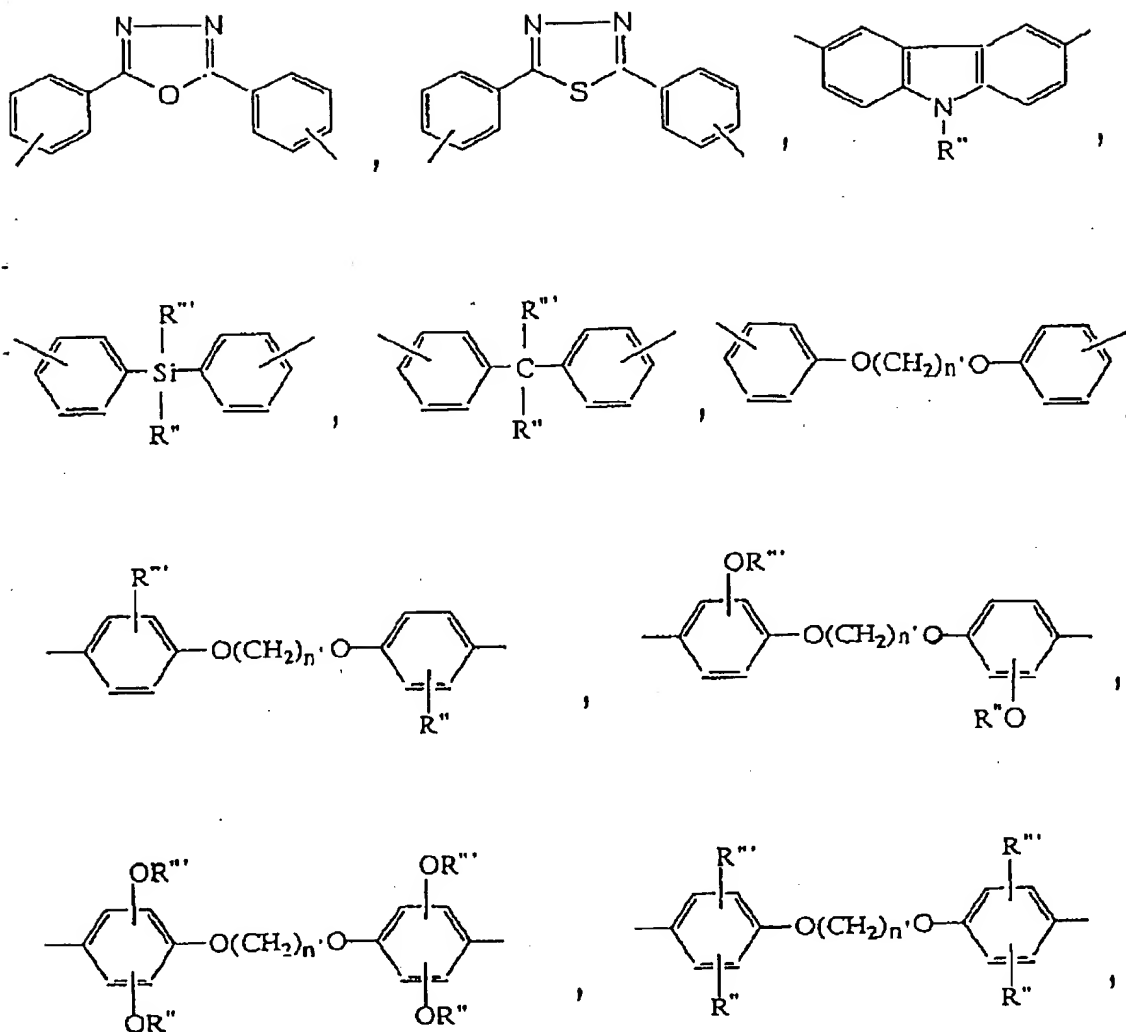
[Formula 5]

- (CH₂)_{n'} -



[0010]

[Formula 6]

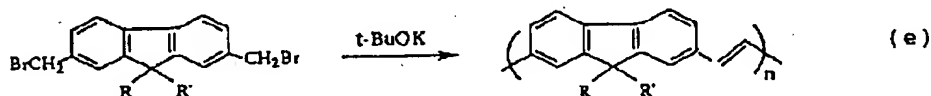
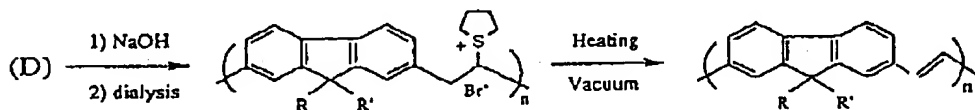
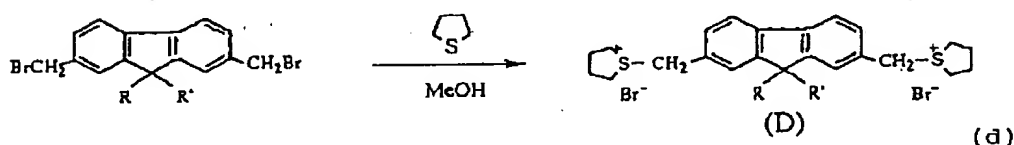
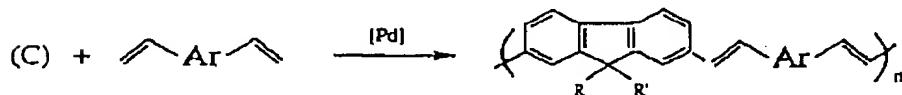
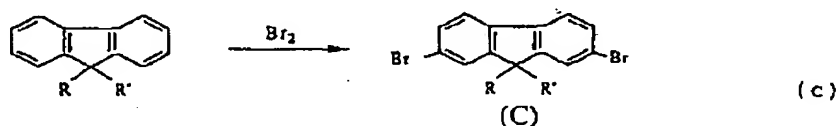
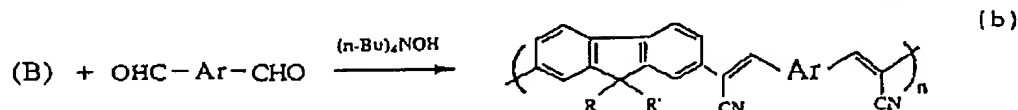
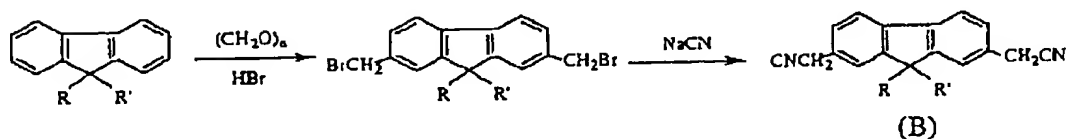
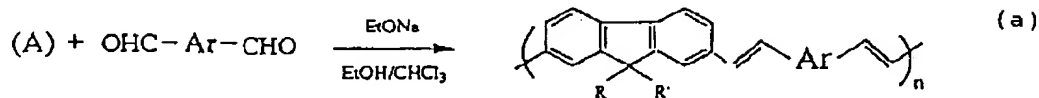
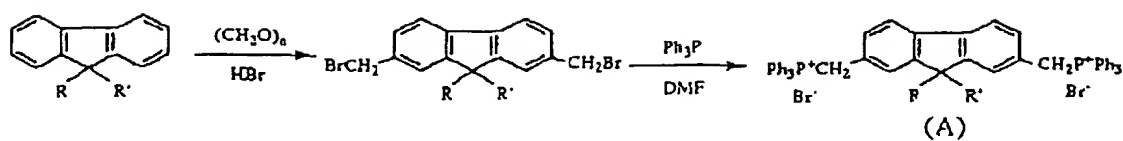


[0011] Expressing the radical shown by (' expresses R'' and the aryl group whose number is 6-18, an aryloxy group, or an aralkyl radical, respectively, and a carbon number expresses [the alkyl group to 22 pieces, a cycloalkyl radical, an alkoxy group, an alkoxyalkyl group, an alkoxy alkoxyalkyl group, an alkoxy alkoxy alkoxyalkyl group, and a carbon number] R'' of integers of 1-22 among a formula, as for n'), n expresses the integer of 1-2,000.

[0012] Here, although especially the degree of polymerization of the copolymer of this invention is not limited, in the point that there is fusibility to an organic solvent and a thin film can form by spin coating or the casting approach, as a degree of polymerization, 1-2,000 are desirable and it is still more desirable that it is 3-1,000. The Wittig (Wittig) reaction which especially the manufacture approach of a copolymer of having conjugated double bond is not limited, either, for example, is a well-known approach (J.Am.Chem.Soc., 82, p.4669, Org.React., 25, and p.73) (refer to the following (1977) reaction formula (a)). The inside of a formula, R , R' , and Ar And n is the same as the aforementioned definition. reaction-formula (b) - (e) — also setting — the same — KUNEBENAGERU (Knoevenagel) condensation (J.Org.Chem., 25, and p.813 (1960) —) Maacromolecules, 27, and p.3009 (refer to the following (1994) reaction formula (b)), the approach (Org.React., 27, and p.345 (1981) —) of Heck (Heck) by the palladium catalyst Macromolecules, 28, and p.6410 (1995), (refer to the following reaction formula (c)) the approach (U.S. Pat. No. 3,401,152, J.Chem.Soc., Chem. Commun., and p.32 (1992) —) using a precursor Science, 269, and p.376 (refer to the following (1995) reaction formula (d)), and the reaction (J.Polym.Sci., Part A-1.4, and p.1337 (1996) —) using a strong base like potassium-tert butoxide Synth, Met., 62, p.35, etc. can be used for this invention (refer to the following (1994) reaction formula (e)).

[0013]

[Formula 7]



[0014] When it explains to a detail more, generally the monomers with which manufacture of the copolymer using a Wittig reaction is presented are phosphonium salt and dialdehyde, and make them react under a strong base nature catalyst like sodium or alkyl lithium using an organic solvent like ethanol.

[0015] In this invention, in the fluorene system phosphonium salt which has a substituent in a screw (BUROMO (or chloro) methyl) fluorene or its part as phosphonium salt, on the other hand, although various dialdehydes can be used, as dialdehyde, all the fluorene system phosphonium salt displayed by the general formula (I) after a polymerization and saturation aliphatic series, or aromatic series dialdehyde is included. Specifically as fluorene system phosphonium salt Like the triphenyl phosphonium salt of a 2, triphenyl phosphonium salt [of 7-screw (bromomethyl) fluorene], 2, and 7-screw

(bromomethyl)-9-alkyl fluorene A carbon number The alkyl group to 22 pieces, [the hydrogen 1 individual of nine locations of a fluorene] A cycloalkyl radical, an alkoxy group, an alkoxyalkyl group, an alkoxy alkoxyalkyl group, An alkoxy alkoxy alkoxyalkyl group, the aryl group whose carbon number is 6-18 pieces, The phosphonium salt of the fluorene permuted by the aryloxy group or the aralkyl radical, Like the triphenyl phosphonium salt of 2, the 7-screw (bromomethyl) -9, and 9-dialkyl fluorene, and the hydrogen 2 individual of nine locations of a fluorene A carbon number, respectively The alkyl group to 22 pieces, a cycloalkyl radical, an alkoxy group, The phosphonium salt of the fluorene permuted by the aryl group an alkoxyalkyl group, an alkoxy alkoxyalkyl group, an alkoxy alkoxy alkoxyalkyl group, and whose carbon number are 6-18 pieces, the aryloxy group, or the aralkyl radical is mentioned. The saturation aliphatic series dialdehyde or the phthalaldehyde like [as dialdehyde] glutaraldehyde on the other hand, A carbon number like the aromatic series dialdehyde which does not have a substituent like an isophthal aldehyde and a terephthal aldehyde or 1, the 4-dialkyl -2, and 5-diformyl benzene The alkyl group to 22 pieces, A cycloalkyl radical, an alkoxy group, or the aryl group of 6-18 carbon numbers, The aromatic series dialdehyde by which the hydrogen 2 individual of a ring was permuted by the aryloxy group or the aralkyl radical, A 2 and 2'- or 3, and 3'- or 4, and 4'-diformyl biphenyl, 2 and 2'- or 3, and 3'- or 4, and 4'-diformyl diphenyl ether, diphenyl SURUFIDO, or a diformyl biphenyl derivative like diphenyl alkylamine, A terphenyl dialdehyde compound like a 2, 7-diformyl fluorene derivative, 4, and 4'-diformyl terphenyl, 1, a naphthalene dialdehyde compound like 8-diformyl naphthalene, 1 and 8- or 3, an anthracene dialdehyde compound like 6-diformyl anthracene, 2, 6-diformyl pyridine, 2, 5-diformyl furan, 2, 5-diformyl thiophene, 3, 4-dialkyl -2, 5-diformyl thiophene, 5, and 5'-diformyl -2, 2'-bithiophene, The 1, 4-dialkyl -2, 5-diformyl pyrrole, 1, and 1'-dialkyl -5, 5'-diformyl -2, 2'-bipyrrole, 5 and 5'-diformyl -1, 1'-bipyrrole, 3, 6-diformyl dibenzofuran, 3, 6-diformyl dibenzo thiophene, 2, 5-screw (2-, 3-, or 4-formylphenyl) - 1, 3, 4-diphenyl thiadiazole, There is a diformyl carbazole by which a carbon number like alkyl -3 and 6-diformyl carbazole was permuted by the alkyl group or cycloalkyl radical to 22 pieces.

[0016] Moreover, the screw (cyano methyl) fluorene which replaced with the aforementioned fluorene system phosphonium salt, and cyanides like a sodium cyanide was made to react to the aforementioned screw (bromomethyl) fluorene and its derivative as a monomer with which manufacture of the copolymer using KUNEBENAGERU (Knoevenagel) condensation is presented, and was manufactured, and its derivative can be used, and he is aforementioned Wittig (Wittig) as dialdehyde. The dialdehyde compound used at the reaction can be used as it is. This copolymerization reaction makes two monomer compounds react using an organic solvent like a tetrahydrofuran or toluene under a strong base nature catalyst like tetra-n-butyl ammonium hydroxide or potassium-tert butoxide.

[0017] Furthermore, Heck by the palladium catalyst (Heck) Generally an approach is palladium acetate and a tree about bromination or an iodination aromatic compound, and an aromatic series divinyl compound in a basic solvent like dimethylformamide. It uses together with o-tolyl HOSUFEN and an amine compound like tributylamine, and a condensation reaction is carried out. Therefore, the bromination or the iodination aromatic compound concerning this invention can add a bromine or iodine to the aforementioned fluorene and its derivative, and bromination or the derivative which carried out iodination can be used for it as it is. For example, if fluorene, 9-alkyl or 9, and 9-dialkyl fluorene is processed with a bromine in dimethylformamide or a chloroform solvent, the fluorene compound with which 2 and 7-dibromo fluorene or the hydrogen of the nine locations was permuted by the alkyl group will be obtained. On the other hand, as an aromatic series divinyl compound, m-divinylbenzene, p-divinylbenzene, 2, and 2'- or 3, and 3'- or 4, and 4'-divinylbiphenyl, 2, 5-divinyl thiophene and 2, and 6-divinyl naphthalene etc. carries out the Wittig reaction of the aforementioned dialdehyde compound, and is obtained, for example.

[0018] Furthermore, by the approach using the aforementioned precursor, if a screw (chloro or bromomethyl) fluorene and its derivative are made to react with tetrahydrothiophene in a methanol solvent in relation to this invention as a monomer, a tetrahydrothiophene salt can be obtained easily. Therefore, the screw (chloro or bromomethyl) fluorene obtained by the aforementioned Wittig reaction and its derivative can be used as one side of the monomer of this invention as it is. After carrying out a

polymerization reaction and dialyzing this tetrahydrothiophene salt in water or a methanol solvent, if it heats in a vacuum, the polymer of this invention will be obtained.

[0019] Moreover, by the approach of carrying out a polymerization using a strong base, if the screw (chloro or bromomethyl) fluorene of the above concerning this invention and its derivative are made to react by strong base like potassium-tert-butoxide or n-butyl lithium in toluene or a tetrahydrofuran solvent, a polymer will be obtained easily. Therefore, the aforementioned screw (chloro or bromomethyl) fluorene and its derivative can be used as it is as a monomer also by this approach.

[0020] Furthermore, since the polymer concerning this invention which forms a luminous layer is placed between an anode plate and cathode, namely, it can use together with the ingredient (JP,2-135361,A, JP,3-152184,A, and JP,6-207170,A) of the hole-injection layer which it can use for the thing of a general component configuration, and is a well-known fact, and an electron injection layer like an anode plate / luminous layer / cathode and can also constitute, the configuration of the EL element using the fluorene system macromolecule of this invention is not limited especially about a component configuration. A component configuration called an anode plate / hole-injection layer / luminous layer / electron injection layer / cathode is also included by the EL element of this invention. In this case namely, as an anode plate On the glass as a transparent support substrate, a transparent plastic, or a quartz, ITO as an electrode material, gold, copper, the tin oxide, a metal like a zinc oxide, or a metallic oxide, The ingredient with which an organic-semiconductor compound like polypyrrole, the poly aniline, and the poly thiophene was usually covered by the thickness of 10nm - 1 micro is used. On the other hand, or as cathode Sodium, magnesium, calcium, aluminum, an indium, silver, gold, metals like copper, or those alloys can be used. A hole-injection layer is polyvinyl-carbazole, 2, and 5-screw (4-diethylaminophenyl). - 1, 3, 4-OKISA diazole, Or N, N'-diphenyl-N, N'-(3-methylphenyl)-1, and 1'-biphenyl-4,4'-diamine (TPD) as an electron injection layer — tris (eight quinolinol) aluminum and 2-(4-tert-butylphenyl)-5-(4-biphenyl)- 1, 3, and 4-OKISA diazole — 2, 4, and 7-trinitro full — me — a well-known compound like non — respectively — vacuum deposition, spin coating, casting, or LB — what is necessary is just to form these thin films on an anode plate or cathode using the well-known thin film formation approaches, such as law

[0021] And the luminescence polymer of this invention can also be used, mixing with PPV of the luminescence polymer with which the aforementioned hole-injection layer and an electron injection layer, or this invention is different from each other, and fusibility, and an existing luminescence polymer like a PTh derivative. For example, after melting a polyvinyl carbazole and Pori (1, the 4-hexyloxy phenylene - 2, 5-diyl vinylene) or Pori (3-hexyl thiophene), and the fluorene system giant molecule of this invention to an organic solvent like chloroform, the layer concerned can be made to form in the layer which adjoins it by the spin coating method or the casting method. Here, although not limited especially, to a polyvinyl carbazole, concentration prepares the fluorene system giant molecule of this invention so that it may become 0.1 - 50 % of the weight preferably 0.001% of the weight or more, and as the thickness of a thin film is set to 50nm - 1micro, it is preferably used for it 5nm - 5micro. Moreover, it can dissolve in an organic solvent common in addition to an electron hole transfer layer and an electron transport layer, and the macromolecule in which thin film formation is possible can also be mixed and used for the aforementioned concentration and the range of thickness. As an usable giant molecule, for example, a polymethyl methacrylate, polyacrylic ester, Polystyrene, a polycarbonate, a polyvinyl chloride, polyethylene, Polypropylene, a polyacrylonitrile, a polyvinyl pyrrolidone, polyvinyl alcohol, Polyvinyl acetate, a polyvinyl butyral, a polyvinyl amine, the poly caprolactone, Polyethylene terephthalate, polybutene terephthalate, polyurethane, ABS, polysulfone, thermoplastics like a polyvinyl fluoride, Or there are polyacetal, a polyamide, polyimide, polyester, alkyd resin, urea resin, furan resin, nylon, melamine resin, phenol resin, silicone resin, general-purpose resin like an epoxy resin, etc.

[0022]

[Embodiment of the Invention] Although the EL element using the fluorene system alternating copolymer for EL elements and it concerning this invention is hereafter explained to a detail based on an example, this invention is not limited to these examples.

[0023]

[Example]

The monomer used for monomer composition this invention may use what kind of monomer, as long as a polymer is the macromolecule with which are satisfied of a general formula (I). Moreover, although not indicated below, generally it could compound easily, or a well-known compound, the analogue, and the monomer that can be purchased were compounded and purchased by the well-known approach and the similar approach, and was used for manufacture of a polymer.

[0024] 1L equipped with 2, the synthetic agitator of a 7-screw (bromomethyl)-9-hexyl fluorene, the thermometer, and the reflux capacitor 9-hexyl fluorene 50.0g (0.2 mols), paraformaldehyde 60g (2.0 mols), and 500g of 30% of HBr nitric-acid solutions were put into the three-lot flask, and it was made to react at the temperature of 60 degrees C for 24 hours. Temperature was reduced to ordinary temperature after the reaction, and the solid-state of thin yellow was deposited. After filtering this, water and a methanol washed several times, it was made to fully dry in 40-degree C vacuum oven, and the solid-state with a white of 74g (85% yield) was obtained. The melting point was 143-145 degrees C. 1 H-NMR spectrum (solvent CDCl₃), d 0.88 (t, 3H, CH₃), 1.25 (m, 8H, CH₂), 2.01 (m, 2H, CH₂), 3.98 (t, 1H, CH), 4.63 (s, 4H, CH₂Br), 7.39-7.72 (m, 6H, aromatic series)

[0025] 1L equipped with the synthetic agitator, thermometer, and reflux capacitor of the triphenyl phosphonium salt of a 2 and 7-screw (bromomethyl)-9-hexyl fluorene 2 and 7-screw (bromomethyl)-9-hexyl fluorene 43.6g (0.1 mols), triphenyl phosphine 78.7g (0.3 mols), and N.N-dimethylformamide 500mL were put into the three-lot flask, and it was made to react at reflux temperature for 12 hours. 3L which temperature was reduced and was subsequently stirred to ordinary temperature after the reaction It was gradually dropped into the ethyl ether solvent, and the white solid-state was deposited. After filtering this, ethyl ether washed several times, it was made to fully dry in 40-degree C vacuum oven, and the solid-state with a white of 92.2g (96% yield) was obtained.

1 H-NMR spectrum (solvent CDCl₃) and d 0.25 (br, 3H, CH₃), 1.60-1.24 (m, 10H, CH₂), 2.83 (t, 1H, CH), 5.66-5.76 (d, 4H, and CH₂Br), 6.76-7.11 (m, 6H, fluorenyl aromatic series), 7.49-7.81 (m, 30H, aromatic series)

[0026] 1L equipped with 2, the 7-screw (bromomethyl) -9, the synthetic agitator of 9-dihexyl fluorene, the thermometer, and the reflux capacitor 9 and 9-dihexyl fluorene 33.4g (0.1 mols), paraformaldehyde 30g (1.0 mols), 30% of HBr nitric-acid solution of 300g, and 120g of 48% of HBr water solutions were put into the three-lot flask, and it was made to react at 60 degrees C for 24 hours. After reducing temperature to ordinary temperature after the reaction and diluting this resultant with the cold water of 500mL, it extracted 3 times in the dichloromethane of 200mL. After setting the extracted this organic solution, it washed with water, saturation NaHCO₃ water solution, and salt water again. Then, the obtained organic solution was dried with sulfuric anhydride magnesium, the solvent was evaporated after filtration, and the viscous liquid was obtained. This liquid was refined using the silica gel column (ethyl acetate/hexane = 1/10 of mixed solutions), the solvent was evaporated, and the liquid with 44.2g (85% yield) transparent and colorless viscosity was obtained.

1 H-NMR spectrum (solvent CDCl₃), d 0.59 (br, 6H, CH₃), 0.72-1.04 (m, 16H, CH₂), 1.95 (m, 4H, CH₂), 4.60 (s, 4H, CH₂Br), 7.33-7.62 (m, 6H, aromatic series)

[0027] 1L equipped with the synthetic agitator, thermometer, and reflux capacitor of the triphenyl phosphonium salt of 2, the 7-screw (bromomethyl) -9, and 9-dihexyl fluorene 2, 7-screw (bromomethyl) -9, and 9-dihexyl fluorene 26.0g (0.05 mols), torr phenyl phosphine 39.3g (0.15 mols), and N.N-dimethylformamide 300mL are put into a three-lot flask, It was made to react at reflux temperature for 12 hours. 1.5L which temperature was reduced and was subsequently stirred to ordinary temperature after the reaction It was gradually dropped into the ethyl ether solvent, and the white solid-state was deposited. After filtering this, ethyl ether washed several times, it was made to fully dry in 40-degree C vacuum oven, and the solid-state with a white of 49.6g (95% yield) was obtained.

1 H-NMR spectrum (solvent CDCl₃) and d 0.11 (br, 6H, CH₃), 0.62-1.09 (m, 16H, CH₂), 1.39 (m, 4H, CH₂), 5.21-5.28 (d, 4H, and CH₂Br), 6.83-7.27 (m, 6H, fluorenyl aromatic series), 7.54-7.75 (m, 30H,

aromatic series)

[0028] Dimethyl sulfoxide 300mL and 2.8g (0.057 mols) of sodium cyanides refined in the three-lot flask of 500mL(s) equipped with the agitator, the thermometer, and the reflux capacitor under a synthetic nitrogen-gas-atmosphere mind of a 2 and 7-screw (cyano methyl)-9-hexyl fluorene were put in, and it stirred, heating at 90 degrees C. Then, heating was made to react at 90 degrees C for 12 hours, if a cyanide dissolves completely after adding gradually stop, 2, and 7-screw (bromomethyl)-9-hexyl fluorene 10g (0.023 mols). in this case, the steps from a color with the red color of this reaction mixture — it changes to deep dark brown. After extracting this reactant 3 times by the dichloromethane of 200mL after reducing temperature to ordinary temperature after reaction termination and adding distilled water of 500mL, and mixing an organic solvent to this extract, it is made to fully dry using sulfuric anhydride magnesium. After filtering this solution, the solvent was evaporated and the orange solid-state was obtained. This was made to recrystallize in ethyl acetate/hexane (1:1), and the 5.7g (76% of yield) solid-state was obtained. The melting point was 130–131 degrees C.

1 H-NMR spectrum (solvent CDCl₃), delta 0.89 (t, 3H, CH₃), 1.25 (m, 8H, CH₂), 2.04 (m, 2H, CH₂), 3.90 (s, 4H, CH₂CN), 4.02 (t, 1H, CH), 7.35–7.79 (m, 6H, aromatic series)

[0029] After melting completely to N,N-dimethylformamide 300mL which refined 9 and 9-dihexyl fluorene 33.4g (0.1 mols) with the three-lot flask of 500mL(s) with an agitator under a synthetic nitrogen-gas-atmosphere mind of 2, 7-dibromo -9, and 9-dihexyl fluorene, 48g (0.3 mols) of bromines was added gradually. Subsequently, after flowing into the water of 500mL, extracting 3 times by diethylether of 200mL(s), after making it react in ordinary temperature for 12 hours, and mixing with an organic solvent, it washed continuously with a sodium-thiosulfate water solution and salt water, the organic layer was separated, and it was made to fully dry using sulfuric anhydride magnesium. After filtering this solution, the solvent was evaporated and the solid-state of thin yellow was obtained. This was made to recrystallize in a hexane and the crystal solid-state with a white of 43.8g (89% yield) was obtained. The melting point was 61–62 degrees C.

1 H-NMR spectrum (solvent CDCl₃), delta 0.55 (br, s, 6H, CH₃), 0.73–1.03 (m, 16H, CH₂), 1.90–1.94 (m, 4H, CH₂), 7.41–7.53 (m, 6H, aromatic series)

[0030] 1L equipped with 2, the synthetic agitator of a 7-screw (bromomethyl)-9-[2-[2-(2-methoxyethoxy) ethoxy] ethyl] fluorene, the thermometer, and the reflux capacitor 9-methoxyethoxy ethoxyethyl fluorene 31.2g (0.1 mols), paraformaldehyde 30g (1.0 mols), 30% of HBr nitric-acid solution of 300g, and 120g of 48% of HBr water solutions were put into the three-lot flask and it be made to react at 60 degrees C for 24 hours. After reducing temperature to ordinary temperature after the reaction and diluting a reactant with the cold water of 500mL, it extracted 3 times by the dichloromethane of 200mL. After mixing the extracted this organic solution, they are water and saturation NaHCO₃ again. It washed continuously with a water solution and salt water, the organic layer was separated, and it was made to dry enough using sulfuric anhydride magnesium. After filtering this solution, the solvent was evaporated and the viscous liquid of thin yellow was obtained. This liquid was refined using the silica gel column (ethyl acetate/hexane = one fourth of mixed solutions), the solvent was evaporated, and the liquid with 39.8g (80% yield) transparent and colorless viscosity was obtained.

1 H-NMR spectrum (solvent CDCl₃), delta 2.28 (m, 3H, OCH₃), 3.41–3.71 (m, 12H, OCH₂CH₂), 4.09 (t, 1H, CH), 4.60 (s, 4H, CH₂Br), 7.25–7.71 (m, 6H, aromatic series)

[0031] 2, the synthetic agitator of the triphenyl phosphonium salt of a 7-screw (bromomethyl)-9-[2-[2-(2-methoxyethoxy) ethoxy] ethyl] fluorene, 1L equipped with the thermometer and the reflux capacitor In a three-lot flask, 2, 7-screw (bromomethyl)-9-[2-[2-(2-methoxyethoxy) ethoxy] ethyl] fluorene 24.9g (0.05 mols), Triphenyl phosphine 39.3g (0.15 mols) and N,N-dimethylformamide 300mL were put in, and it was made to react at reflux temperature for 12 hours. 1.5L which temperature was reduced and was stirred to ordinary temperature after the reaction After having been gradually dropped into the ethyl ether solvent, depositing the white solid-state and filtering it, ethyl ether washed several times, it was made to fully dry in 40-degree C vacuum oven, and the solid-state with a white of 48.5g (95% yield) was obtained.

¹H-NMR spectrum (solvent CDCl₃), delta 1.22–1.41 (m, 2H, CH₂), 2.16–2.42 (br, s, 3H, OCH₃), 3.41–3.71 (m, 10H, OCH₂CH₂), 4.18 (t, 1H, CH), 5.58–5.81 (d, 4H, and CH₂Br), 6.81–7.22 (m, 6H, fluorene aromatic series), 7.27–7.84 (m, 30H, aromatic series)

[0032] 1L equipped with the agitator, the thermometer, and the reflux capacitor under a synthetic nitrogen-gas-atmosphere mind of N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl]-3 and 6-diformyl carbazole. After putting dimethyl formaldehyde 191g (2.61 mols) and 1,2-dichloroethane 100mL into the three-lot flask and fully cooling to 0 degree C, the 197.6 g (1.29 mols) phosphoryl chloride (Phosphorus Oxychloride) was gradually dropped at this. Subsequently, after carrying out the temperature up of this reaction mixture and stirring it to ordinary temperature for 1 hour, it cooled to 0 degree C again, and N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl] carbazole 21.0g (0.067 mols) diluted by this at 1,2-dichloroethane 30mL was added gradually. After carrying out the temperature up of the 1 hour after reaction temperature and making it react to 90 degrees C for 24 hours, temperature is again reduced to ordinary temperature, and it is 1.5L. After diluting with iced water, it extracted 3 times in the dichloromethane of 200mL. After mixing the extracted this organic solution, they are water and saturation NaHCO₃ again. It washed continuously with a water solution and salt water, the organic layer was separated, and it was made to fully dry using sulfuric anhydride magnesium. After filtering this solution, the solvent was evaporated and the viscous yellow liquid was obtained. This liquid was made to recrystallize 3 times in little ethyl acetate, and the solid-state with a thin yellow of 11.1g (45% yield) whose melting point is 108–109 degrees C was obtained.

¹H-NMR spectrum (solvent CDCl₃), delta 3.48–3.56 (m, 11H, OCH₂CH₂, and OCH₃), 3.98 (t, 2H, OCH₂), 4.61 (t, 2H, NCH₂), 7.62 (d, 2H, aromatic series), 8.13 (d, 2H, aromatic series), 8.68 (s, 2H, aromatic series), 10.15 (s, 2H, CHO) [0033] Synthetic example 1 Pori of a polymer () [a fluorene -2,] [7-diyl vinylene-N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl] carbazole -3 and 6-diyl vinylene, in a 100mL flask with an agitator 2, 1.75g of triphenyl phosphonium salts of 7-screw (bromomethyl) fluorene (2-methoxyethoxy) (2mmol) and N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl]-3 and 6-diformyl carbazole 0.74g (2mmol) are put in. After melting completely to dehydrated ethanol 60mL and chloroform 20mL, metallic sodium takes with a syringe 2.3g of solutions dissolved 5% to dehydrated ethanol, and trickles them into this gradually at it. Subsequently, 0.1 Ns after making it react in ordinary temperature for 12 hours Hydrochloric-acid water-solution 1mL was put in, the reaction was ended, and the depositing solid-state was filtered. Washed this solid-state with the methanol, it was made to fully dry in 40-degree C vacuum oven, and the title polymer of a 0.82g yellow solid-state was obtained. The results of having used the tetrahydrofuran as the solvent for this polymer, and having measured weight average molecular weight and molecular weight distribution by GPC, using polystyrene as a primary standard were 2,700 and 1.69, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 3.3–4.0 (br, d, fluorene - CH₂ and carbazole-alkoxy), 4.3–4.6 (br, s, NCH₂), 6.5–8.4 (br, m, vinyl, and aromatic series)

[0034] By the same approach as the synthetic example 1 of example 2 Pori (9-hexyl fluorene -2, the 7-diyl vinylene-N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl] cull bar -3, 6-diyl vinylene) The result to which the polymerization of 1.92g (2mmol) of triphenyl phosphonium salts of a 2 and 7-screw (bromomethyl)-9-hexyl fluorene and the N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl]-3 and 6-diformyl carbazole 0.74g (2mmol) was carried out, The title polymer of a 0.86g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 5,900 and 1.87, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.6–2.2 (br, m, fluorene-aliphatic series), 3.4–4.0 (br, d, fluorene-CH, a fluorene, a carbazole, and alkoxy), 4.3–4.6 (br, s, NCH₂), 6.6–8.3 (br, m, vinyl, and aromatic series)

[0035] By the same approach as the synthetic example 1 of example 3 Pori (9 and 9-dihexyl fluorene -2, the 7-diyl vinylene-N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl] cull bar -3, 6-diyl vinylene) 2.09g (2mmol) of triphenyl phosphonium salts of 2, the 7-screw (bromomethyl) -9, and 9-dihexyl fluorene, and N-[2-[2-(2-methoxyethoxy) ethoxy] ethyl]-3 and 6-diformyl carbazole 0.74g (2mmol) As a result of carrying out

a polymerization, the title polymer of a 0.92g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 11,400 and 2.04, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.6–2.2 (br, m, fluorene–aliphatic series), 3.3–3.9 (br, d, carbazole–alkoxy), 4.3–4.6 (br, s, NCH₂), 6.6–8.4 (br, m, vinyl, and aromatic series)

[0036] By the same approach as the synthetic example 1 of example 4 Pori (the 9–[2–[2–(2–methoxyethoxy) ethoxy] ethyl]–fluorene –2, the 7–diyl vinylene–N–[2–[2–(2–methoxyethoxy) ethoxy] ethyl] cull bar –3, 6–diyl vinylene) 2, 7–screw (Bromomethyl) –9–[2–[2– The result to which the polymerization of 2.05g (2mmol) of triphenyl phosphonium salts of an ethoxy] ethyl] fluorene and the N–[2–[2–(2–methoxyethoxy) ethoxy] ethyl]–3 and 6–diformyl carbazole 0.74g (2mmol) was carried out, (2–methoxyethoxy) The title polymer of a 0.81g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 2,900 and 1.41, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 2.1–2.4 (br, s, fluorene – CH₂), 3.2–3.9 (br, m, fluorene – CH, fluorene and carbazole–alkoxy), 4.3–4.6 (br, s, NCH₂), 6.5–8.4 (br, m, vinyl, and aromatic series)

[0037] Example 5 Pori (— nine — hexyl — a fluorene — two — seven — diyl — one — cyano — vinylene — N — { — two — [— two — (2–methoxyethoxy) — ethoxy —] — ethyl — } — a carbazole — three — six — diyl — one — cyano — vinylene —) — composition — nitrogen gas atmosphere — mind — the bottom — — an agitator — with — 100 — mL — a flask — 2 — 7–screw After melting completely to tetrahydrofuran 20mL which refined (cyano methyl)–9–hexyl fluorene 0.66g (2mmol) and N–[2–[2–(2–methoxyethoxy) ethoxy] ethyl]–3 and 6–diformyl carbazole 0.74g (2mmol), — It cooled to 78 degrees C. It is 1.0 mols to this. Methanol 0.04mL containing hydroxylation tetra—n–butyl ammonium was dropped with the micro syringe. Subsequently, after having carried out the temperature up of the temperature gradually to 50 degrees C, having made it react after 30 minutes for 12 hours, putting in 0.1N hydrochloric–acid water–solution 1mL and terminating a reaction, the methanol of 250mL(s) was gradually filled with this reaction mixture, and the solid-state was deposited. Washed this solid-state with the methanol, it was made to fully dry in 40–degree C vacuum oven, and the title polymer of a 0.80g yellow solid-state was obtained. The results of having used the tetrahydrofuran as the solvent for this solid-state, and having measured weight average molecular weight and molecular weight distribution by GPC, using polystyrene as a primary standard were 38,700 and 4.28, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.5–2.1 (br, m, fluorene–aliphatic series), 3.2–4.0 (br, m, fluorene – CH, and a fluorene and carbazole–alkoxy), 4.3–4.6 (br, s, NCH₂), 6.5–8.2 (br, m, vinyl, and aromatic series)

[0038] Under a synthetic nitrogen–gas–atmosphere mind of example 6 Pori (9 and 9–dihexyl fluorene –2, 7–diyl vinylene–m–phenylenevinylene), with a 100mL flask with an agitator 2, 7–dibromo –9, and 9–dihexyl fluorene 0.98g (2mmol), After melting completely to dimethylformamide 15mL which refined m–divinylbenzene 0.26g (2mmol), acetic–acid palladium 18.2mg, and tree o–tolyl phosphine 124mg, tributylamine 1.4mL was dropped with the syringe. after [subsequently,] having carried out the temperature up of the temperature gradually to 100 degrees C, having made it react after 30 minutes for 24 hours, putting in 0.1N hydrochloric–acid water–solution 1mL and terminating a reaction — this — it flowed into the methanol of reaction mixture 250mL gradually, and the solid-state was deposited. Washed this solid-state with the methanol, it was made to fully dry in 40–degree C vacuum oven, and the title polymer of a 0.81g yellow solid-state was obtained. The results of having used the tetrahydrofuran as the solvent for this polymer, and having measured weight average molecular weight and molecular weight distribution by GPC, using polystyrene as a primary standard were 35,400 and 3.21, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.4–2.2 (br, m, aliphatic series), 6.5–7.8 (br, m, vinyl, and aromatic series)

[0039] By the same approach as the synthetic example 6 of example 7 Pori (9 and 9–dihexyl fluorene –2, 7–diyl vinylene–p–phenylenevinylene), it is 2 and 7–dibromo. – 9 and 9–dihexyl fluorene 0.98g (2mmol)

and p-divinylbenzene 0.26g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.85g yellow solid-state was obtained. The results of having measured weight average molecular weight and molecular weight distribution by the same approach as an example 6 were 26,300 and 2.89, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.5–2.2 (br, m, aliphatic series), 6.5–7.8 (br, m, vinyl, and aromatic series)

[0040] By the same approach as the synthetic example 1 of example 8 Pori (9-hexyl fluorene -2, 7-diyl vinylene-p-phenylenevinylene), they are 1.92g (2mmol) of triphenyl phosphonium salts of a 2 and 7-screw (bromomethyl)-9-hexyl fluorene, and terephthal aldehyde 0.27g (2mmol). As a result of carrying out a polymerization, the title polymer of a 0.62g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 7,200 and 3.41, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.7–2.1 (br, m, aliphatic series), 3.7–4.0 (br, s, fluorene - CH), 6.5–7.8 (br, m, vinyl, and aromatic series)

[0041] By the same approach as the synthetic example 1 of example 9 Pori (9 and 9-dihexyl fluorene -2, 7-diyl vinylene-p-phenylenevinylene), it is 2 and 7-screw (bromomethyl). - 2.09g (2mmol) of triphenyl phosphonium salts, and terephthal aldehyde 0.27g of 9 and 9-dihexyl fluorene (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.68g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 38,200 and 4.45, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.5–2.2 (br, m, aliphatic series), 6.5–7.8 (br, m, vinyl, and aromatic series)

[0042] By the same approach as the synthetic example 1 of example 10 Pori (9-hexyl fluorene -2, 7-diyl vinylene-m-phenylenevinylene), they are 1.92g (2mmol) of triphenyl phosphonium salts of a 2 and 7-screw (bromomethyl)-9-hexyl fluorene, and isophthal aldehyde 0.27g (2mmol). As a result of carrying out a polymerization, the title polymer of a 0.64g thin yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 12,700 and 5.01, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.6–2.2 (br, m, aliphatic series), 3.6–4.0 (br, s, fluorene - CH), 6.4–7.8 (br, m, vinyl, and aromatic series)

[0043] By the same approach as the synthetic example 1 of example 11 Pori (9 and 9-dihexyl fluorene - 2, 7-diyl vinylene-m-phenylenevinylene), it is 2 and 7-screw (bromomethyl). - 2.09g (2mmol) of triphenyl phosphonium salts, and isophthal aldehyde 0.27g of 9 and 9-dihexyl fluorene (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.69g thin yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 43,500 and 4.12, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.4–2.2 (br, m, aliphatic series), 6.5–7.8 (br, m, vinyl, and aromatic series)

[0044] By the same approach as the synthetic example 1 of example 12 Pori (9-hexyl fluorene -2, the 7-diyl vinylene-pyridine -2, 6-diyl vinylene), it is 2, triphenyl phosphonium salt [of a 7-screw (bromomethyl)-9-hexyl fluorene]g [1.92] (2mmol) and 2, and 6-diformyl pyridine 0.27g (2mmol). As a result of carrying out a polymerization, the title polymer of a 0.66g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 20,800 and 5.10, respectively.

¹H-NMR spectrum (solvent CDCl₃), delta 0.7–2.2 (br, m, aliphatic series), 3.7–3.9 (br, s, fluorene - CH), 6.6–7.8 (br, m, vinyl, and aromatic series)

[0045] By the same approach as the synthetic example 1 of example 13 Pori (9 and 9-dihexyl fluorene - 2, the 7-diyl vinylene-pyridine -2, 6-diyl vinylene), it is 2 and 7-screw (bromomethyl). - Triphenyl phosphonium salt [of 9 and 9-dihexyl fluorene]g [2.09] (2mmol) and 2, and 6-diformyl pyridine 0.27g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.68g yellow solid-state was

obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 35,700 and 3.33, respectively. 1 H-NMR spectrum (solvent CDCl₃), delta 0.4–2.2 (br, m, aliphatic series), 6.6–7.8 (br, m, vinyl, and aromatic series)

[0046] By the same approach as the synthetic example 1 of example 14 Pori (9-hexyl fluorene -2, 7-diyl vinylene -2, 2'-bipyrrole - 5 and 5'-diyl vinylene) 2, triphenyl phosphonium salt [of a 7-screw (bromomethyl)-9-hexyl fluorene]g [1.92] (2mmol) and 5, 5'-diformyl -2, and 2'-bipyrrole 0.40g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.78g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 3,500 and 1.75, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.7–2.0 (br, m, aliphatic series), 3.6–3.8 (br, s, fluorene - CH), 5.4–5.8 (br, d, pyrrole - CH₂), 6.0–7.8 (br, m, vinyl, and aromatic series)

[0047] By the same approach as the synthetic example 1 of example 15 Pori (9 and 9-dihexyl fluorene - 2, 7-diyl vinylene -2, 2'-bipyrrole - 5 and 5'-diyl vinylene) 2, 7-screw (bromomethyl) -9, triphenyl phosphonium salt [of 9-dihexyl fluorene]g [2.09] (2mmol) and 5, 5'-diformyl -2, and 2'-bipyrrole 0.40g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.85g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 8,100 and 2.03, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.4–2.1 (br, m, aliphatic series), 5.5–5.8 (br, d, pyrrole - CH₂), 6.1–7.8 (br, m, vinyl, and aromatic series)

[0048] By the same approach as the synthetic example 1 of example 16 Pori (9-hexyl fluorene -2, the 7-diyl vinylene-furan -2, 5-diyl vinylene), it is 2, triphenyl phosphonium salt [of a 7-screw (bromomethyl)-9-hexyl fluorene]g [1.92] (2mmol) and 2, and 5-diformyl furan 0.25g (2mmol). As a result of carrying out a polymerization, the title polymer of a 0.62g **** solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 20,200 and 4.35, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.6–2.2 (br, m, aliphatic series), 3.8–4.0 (br, s, fluorene - CH), 6.2–7.8 (br, m, vinyl, and aromatic series)

[0049] By the same approach as the synthetic example 1 of example 17 Pori (9 and 9-dihexyl fluorene - 2, the 7-diyl vinylene-furan -2, 5-diyl vinylene), it is 2 and 7-screw (bromomethyl). - Triphenyl phosphonium salt [of 9 and 9-dihexyl fluorene]g [2.09] (2mmol) and 2, and 5-diformyl furan 0.25g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.58g dark yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 9,600 and 1.78, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.5–2.1 (br, m, aliphatic series), 6.2–7.8 (br, m, vinyl, and aromatic series)

[0050] By the same approach as the synthetic example 1 of example 18 Pori (9-hexyl fluorene -2, the 7-diyl vinylene-thiophene -2, 5-diyl vinylene), it is 2, triphenyl phosphonium salt [of a 7-screw (bromomethyl)-9-hexyl fluorene]g [1.92] (2mmol) and 2, and 5-diformyl thiophene 0.28g (2mmol). As a result of carrying out a polymerization, the title polymer of a 0.62g dark **** solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 9,300 and 3.89, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.6–2.2 (br, m, aliphatic series), 3.7–4.0 (br, s, fluorene - CH), 6.4–7.8 (br, m, vinyl, and aromatic series)

[0051] By the same approach as the synthetic example 1 of example 19 Pori (9 and 9-dihexyl fluorene - 2, the 7-diyl vinylene-thiophene -2, 5-diyl vinylene), it is 2 and 7-screw (bromomethyl). - Triphenyl phosphonium salt [of 9 and 9-dihexyl fluorene]g [2.09] (2mmol) and 2, and 5-diformyl thiophene 0.28g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.68g dark yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 5,600 and 1.73, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.3–2.1 (br, m, aliphatic series), 6.4–7.7 (br, m, vinyl, and aromatic series)

[0052] the same approach as the synthetic example 1 of example 20 Pori (a fluorene -2, the 7-diyl vinylene-3-hexyl thiophene -2, 5-diyl vinylene) — 2, 1.75g [of triphenyl phosphonium salts of 7-screw (bromomethyl) fluorene] (2mmol) and 3-hexyl -2, and 5-diformyl thiophene 0.45g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.58g red solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 8,600 and 3.43, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.8–1.8 (br, m, aliphatic series), 2.4–2.7 (br, s, thiophene - CH₂), 3.7–4.0 (br, s, fluorene - CH₂), 6.4–7.8 (br, m, vinyl, and aromatic series)

[0053] By the same approach as the synthetic example 1 of example 21 Pori (9 and 9-dihexyl fluorene - 2, the 7-diyl vinylene-3-hexyl thiophene -2, 5-diyl vinylene) 2, 7-screw (bromomethyl) -9, 2.09g [of triphenyl phosphonium salts of 9-dihexyl fluorene] (2mmol) and 3-hexyl -2, and 5-diformyl thiophene 0.45g (2mmol) As a result of carrying out a polymerization, the title polymer of a 0.64g red solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 8,200 and 1.95, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.6–3.0 (br, m, aliphatic series), 6.5–7.8 (br, m, vinyl, and aromatic series)

[0054] By the same approach as the synthetic example 1 of example 22 Pori (9 and 9-dihexyl fluorene - 2, 7-diyl vinylene -2, 2' — bithiophene -5, 5'-diyl vinylene) 2, 7-screw (bromomethyl) -9, triphenyl phosphonium salt [of 9-dihexyl fluorene] g [2.09] (2mmol) and 5, 5'-diformyl -2, and 2'-bithiophene 0.44g (2mmol) The result which carried out the polymerization, The title polymer of a 0.62g dark red solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 14,600 and 2.52, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.6–2.2 (br, m, aliphatic series), 6.6–7.8 (br, m, vinyl, and aromatic series)

[0055] By the same approach as the synthetic example 1 of example 23 Pori (9 and 9-dihexyl fluorene - 2, 7-diyl vinylene -1, 4-JIHEKISOKISHI -2, 5-phenylenevinylene) 2, 7-screw (bromomethyl) -9, triphenyl phosphonium salt [of 9-dihexyl fluorene] g [2.09] (2mmol) and 1, 4-JIHEKISOKISHI -2, and 5-diformyl benzene 0.66g (2mmol) The result which carried out the polymerization, The title polymer of a 0.98g **** solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 13,500 and 3.05, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.4–2.2 (br, m, aliphatic series), 4.0–4.3 (br, s, OCH₂), 6.7–7.8 (br, m, vinyl, and aromatic series)

[0056] By the same approach as the synthetic example 1 of example 24 Pori (9 and 9-dihexyl fluorene - 2, 7-diyl vinylene-diphenyl ether -2, 2'-diyl vinylene), it is 2 and 7-screw (bromomethyl). - Triphenyl phosphonium salt [of 9 and 9-dihexyl fluorene] g [2.09] (2mmol) and 2, and 2'-diformyl diphenyl ether 0.45g (2mmol) As a result of carrying out a polymerization, the polymer of the title of a 0.68g thin yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 18,500 and 3.52, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.5–2.1 (br, m, aliphatic series), 6.7–7.9 (br, m, vinyl, and aromatic series)

[0057] By the same approach as the synthetic example 1 of example 25 Pori (9 and 9-dihexyl fluorene - 2, 7-diyl vinylene - (3-methoxy) -1, the 4-phenylene -1, 6-dioxy hexamethylene - (2-methoxy) -1, 4-phenylenevinylene) 2.09g (2mmol) of triphenyl phosphonium salts, and [[2 and 2'-dimethoxy (4 and 4'-diformyl)] 1 and 6-phenoxy} hexane 0.77g of 2, the 7-screw (bromomethyl) -9, and 9-dihexyl fluorene (2mmol) The result which carried out the polymerization, The title polymer of a 1.08g light green color

solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 8,200 and 2.51, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.3–2.1 (br, m, aliphatic series), 3.6–4.2 (br, m, OCH₂), 6.4–7.7 (br, m, vinyl, and aromatic series)

[0058] By the same approach as the synthetic example 1 of example 26 Pori (9 and 9-dihexyl fluorene – 2, 7-diyl vinylene –1, the 2-phenylene –1, 6-dioxy hexamethylene –1, 2-phenylenevinylene) 2, the 7-screw (bromomethyl) –9, 2.09g (2mmol) of triphenyl phosphonium salts of 9-dihexyl fluorene, [(2 and 2'-diformyl) 1 and 6-JIFENOKISHI] As a result of carrying out the polymerization of the hexane 0.65g (2mmol), the title polymer of a 0.85g apricot color solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 4,500 and 1.79, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.4–2.0 (br, m, aliphatic series), 3.9–4.1 (br, s, OCH₂), 6.6–7.7 (br, m, vinyl, and aromatic series)

[0059] By the same approach as the synthetic example 1 of example 27 Pori (9 and 9-dihexyl fluorene – 2, 7-diyl vinylene –1, the 3-phenylene –1, 6-dioxy methylene –1, 3-phenylenevinylene) 2, the 7-screw (bromomethyl) –9, 2.09g (2mmol) of triphenyl phosphonium salts of 9-dihexyl fluorene, [(3 and 3'-diformyl) 1 and 6-JIFENOKISHI] As a result of carrying out the polymerization of the hexane 0.65g (2mmol), the polymer of the title of a 0.88g thin yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 9,800 and 2.23, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.4–2.0 (br, m, aliphatic series), 3.9–4.1 (br, s, OCH₂), 6.5–7.7 (br, m, vinyl, and aromatic series)

[0060] By the same approach as the synthetic example 1 of example 28 Pori (9 and 9-dihexyl fluorene – 2, 7-diyl vinylene –1, the 4-phenylene –1, 6-dioxy hexamethylene –1, 4-phenylenevinylene) 2, the 7-screw (bromomethyl) –9, 2.09g (2mmol) of triphenyl phosphonium salts of 9-dihexyl fluorene, [(3 and 3'-diformyl) 1 and 6-JIFENOKISHI] As a result of carrying out the polymerization of the hexane 0.65g (2mmol), the title polymer of a 0.86g yellow solid-state was obtained. The results of having measured the weight average molecular weight and molecular weight distribution of this polymer by the same approach as an example 1 were 6,800 and 1.68, respectively.

1 H-NMR spectrum (solvent CDCl₃), delta 0.4–2.1 (br, m, aliphatic series), 3.8–4.1 (br, s, OCH₂), 6.6–7.7 (br, m, vinyl, and aromatic series)

[0061] the proton of the macromolecule manufactured in the example 11 while the structure of the polymer manufactured in the above example was shown in Table 1, respectively, and each carbon 13 nuclear-magnetic-resonance spectrum — it is shown in drawing 1 and drawing 2.

[0062]

[Table 1]

表1 重合体の化学構造

実施例	構 造 式	備 考
1		$R = 2 - [2 - (2 - \text{メトキシエトキシ}) \text{エトキシ}] \text{エチル}$
2		$R_1 = \text{ヘキシル}$ $R_2 = 2 - [2 - (2 - \text{メトキシエトキシ}) \text{エトキシ}] \text{エチル}$
3		$R_1 = R_3 = \text{ヘキシル}$ $R_2 = 2 - [2 - (2 - \text{メトキシエトキシ}) \text{エトキシ}] \text{エチル}$
4		$R_1 = R_2 = 2 - [2 - (2 - \text{メトキシエトキシ}) \text{エトキシ}] \text{エチル}$
5		$R_1 = \text{ヘキシル}$ $R_2 = 2 - [2 - (2 - \text{メトキシエトキシ}) \text{エトキシ}] \text{エチル}$
6		$R_1 = R_2 = \text{ヘキシル}$
7		$R_1 = R_2 = \text{ヘキシル}$

[0063]

[Table 2]

実施例	構 造 式	備 考
8		$R = \text{ヘキシル}$
9		$R_1 = R_2 = \text{ヘキシル}$
10		$R = \text{ヘキシル}$
11		$R_1 = R_2 = \text{ヘキシル}$
12		$R = \text{ヘキシル}$
13		$R_1 = R_2 = \text{ヘキシル}$
14		$R = \text{ヘキシル}$
15		$R_1 = R_2 = \text{ヘキシル}$

[0064]

[Table 3]

実施例	構 造 式	備 考
16		R = ヘキシル
17		R ₁ = R ₂ = ヘキシル
18		R = ヘキシル
19		R ₁ = R ₂ = ヘキシル
20		R = ヘキシル
21		R ₁ = R ₂ = R ₃ = ヘキシル
22		R ₁ = R ₂ = ヘキシル
23		R ₁ = R ₂ = R ₃ = R ₄ = ヘキシル

[0065]

[Table 4]

実施例	構 造 式	備 考
24		R ₁ = R ₂ = ヘキシル
25		R ₁ = R ₂ = ヘキシル
26		R ₁ = R ₂ = ヘキシル
27		R ₁ = R ₂ = ヘキシル
28		R ₁ = R ₂ = ヘキシル

[0066] It asked for the ultraviolet-rays (UV is called Ultraviolet and the following) spectrum and the

photoluminescence (PL is called Photoluminescence and the following) spectrum from the film of a thin film using the polymer manufactured in ultraviolet rays, photoluminescence and the electroluminescence property, and the example of the manufacture above of an EL element. Here, after it made it dissolve in the chloroform solution of 5mL(s) and formation of a thin film refined 0.1g of said polymers using the 0.2micro filter, it was based on the spin coating method which controlled the spin rate so that the thickness of a thin film was set to about 100nm (usually 900 – 1,200rpm). After drying the sample after coating termination in ordinary temperature, first, it asked for UV spectrum and asked for PL spectrum after that using the wavelength of UV peak maximal value. Thus, the obtained result was summarized and displayed on Table 2.

[0067]

[Table 5]

表2 実施例で製造された重合体の特性

実施例	UV (λ_{max} nm)	PL (λ_{max} nm)	T _{deg} * (°C)
1	406	470, 492	212.1
2	408	470	216.5
3	408	466	216.8
5	420	558, 496	314.9
6	382	428, 448	414.4
7	412	480	420.1
8	406	490, 564	414.0
10	368	453	405.7
12	386	551	411.8
13	388	495, 530	421.8
14	392	466	378.2
15	398	467	403.8
23	444	509, 547	383.1
24	368	425, 445	410.4
25	388	458	397.8
26	374	429, 449	408.9
27	380	420, 441	416.9
28	386	447	410.0

* T_{deg} は熱重量分析による重合体の分析開始温度

[0068] As shown in Table 2, the polymer of this invention shows PL peak maximal value (420–564nm) of a large field. That is, the polymer of this invention carries out photoluminescence of various hues. In addition, these UV spectra and PL spectra are shown in drawing 3 – drawing 23.

[0069] Next, the component configuration generally used, i.e., the EL element which consists of an ITO substrate / a luminous layer / an electrode, was manufactured, and EL property was investigated. Here, the luminous layer chose aluminum as an electrode using what mixed the general-purpose giant molecule mentioned above, using the polymer manufactured in the aforementioned example as it is, for example, a polyvinyl carbazole, a PORIMECHIRU meta-acrylic rate, polystyrene, and an epoxy resin with the polymer applied to this invention with a chloroform solvent.

[0070] Like manufacture of the aforementioned UV spectrum and PL spectrum test sample, manufacture of an EL element formed the luminous layer with the spin coating method so that thickness might be set to 100nm on an ITO glass substrate, and it depended it on subsequently to this luminous layer top carrying out vacuum deposition of the aluminum. Thus, in order to search for the voltage-current property of the constituted EL element, current change was measured, changing an electrical potential difference to –10V to 25V, or more than it. As shown in drawing 24 – drawing 31, the electrical potential differences which show that electroluminescence is performed with the critical voltage of the polymer concerning this invention, i.e., the electrical potential difference beyond it, were 10–20V.

Moreover, an electrical-potential-difference-electroluminescence property is shown in drawing 32 - drawing 35 . In order to analyze the light which carried out electroluminescence, the spectrum of the light which penetrates an ITO glass side was measured with the spectroscopy, and the luminescent color phase was defined from the wavelength which shows the maximum luminescence. Furthermore, PL spectrum of the emitter which mixed two or more polymers manufactured by drawing 36 - drawing 39 among the aforementioned example in EL spectrum and the aforementioned general-purpose macromolecule, and the voltage-current property, electrical-potential-difference-electroluminescence property and EL spectrum of an EL element which created this emitter according to the aforementioned configuration were shown in drawing 40 - drawing 46 , drawing 47 - drawing 50 , and drawing 51 -52, respectively. Furthermore, the schematic diagram of a component configuration used by this invention was shown in drawing 53 .

[0071]

[Effect of the Invention] It is effective in the ability to manufacture the macromolecule EL ingredient of the various classes which the electroluminescence devices using the fluorene system alternating copolymer for EL elements and it concerning this invention are simple for the manufacture approach, and clear in the structure of the last matter as explained above, and may be well dissolved in an organic solvent.

[Translation done.]

*** NOTICES ***

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Polymer concerning the example 11 of this invention It is drawing having shown 1 H-NMR spectrum.

[Drawing 2] It is drawing having shown the polymer 13C-NMR spectrum concerning the example 11 of this invention.

[Drawing 3] UV spectrum of the polymer concerning the example 1 of this invention (continuous line.) Hereafter, it is PL spectrum (broken line.) similarly. the following — being the same — it is shown drawing.

[Drawing 4] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 2 of this invention.

[Drawing 5] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 3 of this invention.

[Drawing 6] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 5 of this invention.

[Drawing 7] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 6 of this invention.

[Drawing 8] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 7 of this invention.

[Drawing 9] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 8 of this invention.

[Drawing 10] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 10 of this invention.

[Drawing 11] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 12 of this invention.

[Drawing 12] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 13 of this invention.

[Drawing 13] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 14 of this invention.

[Drawing 14] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 15 of this invention.

[Drawing 15] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 17 of this invention.

[Drawing 16] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 19 of this invention.

[Drawing 17] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 21 of this invention.

[Drawing 18] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 23 of this invention.

[Drawing 19] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the

example 24 of this invention.

[Drawing 20] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 25 of this invention.

[Drawing 21] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 26 of this invention.

[Drawing 22] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 27 of this invention.

[Drawing 23] It is drawing having shown UV spectrum and PL spectrum of a polymer concerning the example 28 of this invention.

[Drawing 24] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 1 of this invention.

[Drawing 25] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 2 of this invention.

[Drawing 26] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 3 of this invention.

[Drawing 27] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 5 of this invention.

[Drawing 28] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 6 of this invention.

[Drawing 29] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 7 of this invention.

[Drawing 30] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 8 of this invention.

[Drawing 31] It is drawing having shown the voltage-current property of the EL element using the polymer concerning the example 10 of this invention.

[Drawing 32] It is drawing having shown the electrical-potential-difference-electroluminescence property of the EL element using the polymer concerning the example 6 of this invention.

[Drawing 33] It is drawing having shown the electrical-potential-difference-electroluminescence property of the EL element using the polymer concerning the example 7 of this invention.

[Drawing 34] It is drawing having shown the electrical-potential-difference-electroluminescence property of the EL element using the polymer concerning the example 8 of this invention.

[Drawing 35] It is drawing having shown the electrical-potential-difference-electroluminescence property of the EL element using the polymer concerning the example 10 of this invention.

[Drawing 36] It is drawing having shown the electroluminescence spectrum of an EL element using the polymer concerning the example 6 of this invention.

[Drawing 37] It is drawing having shown the electroluminescence spectrum of an EL element using the polymer concerning the example 7 of this invention.

[Drawing 38] It is drawing having shown the electroluminescence spectrum of an EL element using the polymer concerning the example 8 of this invention.

[Drawing 39] It is drawing having shown the electroluminescence spectrum of an EL element using the polymer concerning the example 10 of this invention.

[Drawing 40] It is drawing having shown PL spectrum of the mixture film of the polymer and polyvinyl carbazole concerning the example 6 of this invention. (The figure in a box shows the weight fraction of a polymer.) the following — the same —

[Drawing 41] It is drawing having shown PL spectrum of the mixture film of the polymer and polyvinyl carbazole concerning the example 7 of this invention.

[Drawing 42] It is drawing having shown PL spectrum of the mixture film of the polymer and polyvinyl carbazole concerning the example 12 of this invention.

[Drawing 43] It is drawing having shown PL spectrum of the mixture film of the polymer and polymethylmethacrylate concerning the example 6 of this invention.

[Drawing 44] It is drawing having shown PL spectrum of the mixture film of the polymer and polystyrene concerning the example 12 of this invention.

[Drawing 45] It is drawing having shown PL spectrum of the mixture film of the polymer and polymethylmethacrylate concerning the example 12 of this invention.

[Drawing 46] It is drawing having shown PL spectrum of the mixture film of the polymer and epoxy concerning the example 6 of this invention.

[Drawing 47] It is drawing having shown the voltage-current property of the EL element using the mixture film of the polymer (weight fraction 0.25) and polyvinyl carbazole concerning the example 6 of this invention.

[Drawing 48] It is drawing having shown the electrical-potential-difference-electroluminescence property of the EL element using the mixture film of the polymer (weight fraction 0.25) and polyvinyl carbazole concerning the example 6 of this invention.

[Drawing 49] It is drawing having shown the electrical-potential-difference-electroluminescence property of the EL element using the mixture film of the polymer (weight fraction 0.5) and polyvinyl carbazole concerning the example 13 of this invention.

[Drawing 50] It is drawing having shown the electrical-potential-difference-electroluminescence property of the EL element using the mixture film of the polymer (weight fraction 0.5) and polyvinyl carbazole concerning the example 13 of this invention.

[Drawing 51] It is drawing having shown EL spectrum of an EL element using the mixture film of the polymer (weight fraction 0.2) and polyvinyl carbazole concerning the example 6 of this invention.

[Drawing 52] It is drawing having shown EL spectrum of an EL element using the mixture film of the polymer (weight fraction 0.2) and polyvinyl carbazole concerning the example 7 of this invention.

[Drawing 53] It is drawing having shown the example of a configuration of the EL element using the fluorene system alternating copolymer concerning this invention, or the mixture film of this and a general-purpose macromolecule as a luminous layer.

[Translation done.]